A Facile Strategy for Non-fluorinated Intrinsic Low-\(k\) and Low-loss Dielectric Polymers: Valid Exploitation of Secondary Relaxation Behaviors

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Abstract

High-performance low-\(k\) and low-loss circuit materials are urgently needed in the field of microelectronics due to the upcoming Fifth-Generation Mobile Communications Technology (5G Technology). Herein, a facile design strategy for non-fluorinated intrinsic low-\(k\) and low-loss polyimides is reported by fully considering the secondary relaxation behaviors of the polymer chains. A new amorphous non-fluorinated polymer (TmBPPA) with a \(k\) value of 2.23 and a loss tangent lower than 3.94 \(\times 10^{-3}\) at 10\(^4\) Hz has been designed and synthesized, which to the best of our knowledge is the lowest value amongst the non-fluorinated and non-porous polymers reported in literature. Meanwhile, TmBPPA exhibits excellent overall properties, such as excellent thermostability, good mechanical properties, low moisture absorption, and high bonding strength. As high-performance flexible circuit materials, all these characteristics are highly expected to meet the present and future demands for high density, high speed, and high frequency electronic circuit used in 5G wireless networks.

Keywords Polyimides; Low-\(k\); Free volume; Secondary relaxation

INTRODUCTION

Advances in mobile communications and microelectronics are revolutionizing our way of life. With the development of electronic products in the trend of lighter, thinner, shorter, and smaller, the integration density of flexible circuit boards is getting increasingly higher.\(^{[1-3]}\) On the other hand, with the fast development of the emerging Fifth-Generation Mobile Communications Technology (5G Technology), signal transmission continues to develop in the direction of high frequency and high speed.\(^{[4,5]}\) Both of the above technologies require high-performance insulated materials with low dielectric constant (\(D_k < 2.6\)) and low loss tangent (\(D_t < 5.0 \times 10^{-3}\)) properties to reduce the resistance-capacitance delay (RC delay), the line-to-line crosstalk noise, and the power dissipation, thus to ensure the speed, the integrity, and the accuracy of signal transmission and to improve the service life of electronic components.\(^{[6-8]}\) In principle, there are two strategies to reduce the \(D_k\) and \(D_t\) values of polymer materials.\(^{[9-14]}\) One is to decrease the polymer density, which has the strongest effect on the concentration of polarizable components and the \(k\) value.\(^{[15-21]}\) As a result, decreasing the polymer density by deliberate introduction of porosity has been the main method used by the semiconductor industry to decrease \(k\) below 3.0 (which can be as low as 1.16).\(^{[19]}\) However, the pores with uncontrolled size and distribution exhibit high moisture absorption and usually collapse under high temperature, resulting in deterioration of the dielectric properties.\(^{[22-30]}\) Another strategy is the introduction of strongly electronegative atoms, such as fluoride, into the polymeric structure to reduce the polarizability.\(^{[27-30]}\) The \(k\) value of fluorinated polymers can reach 2.30, but the poor adhesion between the fluorinated polymer and the substrate remains a significant challenge.\(^{[31]}\) Therefore, the development of non-fluorinated intrinsic polymer circuit materials with low-\(k\) and low-loss properties still requires much more efforts.

In general, the most effective way to reduce the \(D_k\) and \(D_t\) values of non-fluorinated and non-porous polymeric materials is to increase the intrinsic free volume. This is because the additional free volume in the polymer introduces more ultra-low-\(k\) air component and subsequently dilutes the polar group concentration and weakens the interactions between...
the polymer chains. Most of the prior-art has focused on introducing bulky side-groups into the polymeric structure in order to enlarge the free volume between polymer chains, but the complicated polymeric structure and high manufacturing cost make it difficult to realize commercial production and industrial application. Therefore, a facile and effective chemical structure design strategy to increase the free volume of polymers is a vital approach to obtain non-fluorinated intrinsic low-k polymers. In contrast to the static molecular design approach reported in literature, herein, a brand-new molecular design strategy is proposed to obtain a high performance intrinsic non-fluorinated low-k polymer by fully considering the secondary relaxation of the polymer chains, especially the β relaxation. For polymeric systems, when the environment temperature is below the glass transition temperature (T_g), the segmental motion is frozen; however, the side-group is still rotatable (known as the secondary relaxation or β relaxation that refers to the torsion of groups in the polymer backbone or the rotation of the pendant group), which can greatly affect the intrinsic free volume.

In order to specifically manipulate the secondary relaxation behavior of the polymer chains, we have designed a new non-fluorinated intrinsic low-k polymer (TmBPPA) (Fig. 1a) in order to improve the intrinsic free volume via the rotation of homocyclic aromatic rings in the side-groups. As-prepared TmBPPA film exhibits a k value of 2.23 with a loss tangent of 3.94 × 10^{-3} at 10^4 Hz. Moreover, the film shows high thermo-stability with T_g of 352 °C, 5 wt% decomposition temperature of 579 °C, and a residue rate of 67% at 800 °C under N_2, which means that it certainly meets the requirement of Cu damascene metallization in microelectronics fabrication. To the best of our knowledge, the k value of TmBPPA is the lowest reported amongst the non-fluorinated and non-porous polyimides. Besides, our product also exhibits outstanding thermo/mechanical properties.

**EXPERIMENTAL**

**Materials**

3-Bromoaniline, 4-bromoaniline, 1-fluoro-4-nitrobenzene, 4-biphenylboronic acid, aniline, and cesium fluoride were purchased from Aladdin Industrial Corporation and used as received. Aliquat 336 (tricaprylylmethylammonium chloride) and tetra-kis(triphenylphosphine) palladium (Pd(PPh_3)_4) were purchased from J&K company and used as received. Pyromellitic dihydride (PMDA) was purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd. and was heated at 150 °C under vacuum for 12 h prior to use. Chromatographically pure dimethyl formamide (DMF) was purified by distillation under an inert nitrogen atmosphere. All other solvents and reagents as analytical grade were purchased from Guangzhou Dongzheng Company and used without further purification.

**Synthesis and Characterization of TmBPPA Film**

**Synthesis of 3-bromo-N,N-bis(4-nitrophenyl)aniline (N-TmBr)**

As shown in Scheme 1, 3-bromoaniline (5.160 g, 30 mmol), CsF (9.120 g, 60 mmol), 1-fluoro-4-nitrobenzene (10.582 g, 75 mmol), and DMSO (150 mL) were added into a 500 mL 3-neck round-bottom flask and reacted for 24 h at 150 °C under nitrogen. After pouring into 500 mL of cold saturated salt water, yellow precipitates were collected and then purified by chromatography on silica gel with dichloromethane/hexane as an eluent. The purified product is light yellow needle type crystals with a yield of 65%.

\[ \text{H-NMR} \ (400 \text{ MHz, } d-\text{DMSO}, \delta, \text{ ppm}): \ 8.21 \ (d, \ J = 9.2 \text{ Hz}, 4H), 7.56 \ (d, \ J = 7.3 \text{ Hz}, 1H), 7.50 \ (t, \ J = 1.9 \text{ Hz}, 1H), 7.46 \ (t, \ J =

![Fig. 1](https://doi.org/10.1007/s10118-020-2339-4)
The reaction was followed by refluxing under nitrogen for 24 h. After removing the aqueous layer, the yellow precipitates were collected by rotary evaporation and purified by chromatography on silica gel with dichloromethane/hexane as an eluent. The purified product is grey crystals with a yield of 72%. $^1$H-NMR (400 MHz, d-DMSO, δ, ppm): 7.69 (t, J = 7.9 Hz, 4H), 7.55−7.42 (m, 4H), 7.36 (t, J = 7.3 Hz, 1H), 7.17 (t, J = 7.9 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.89 (d, J = 8.5 Hz, 5H), 6.58 (t, J = 11.8 Hz, 5H), 5.03 (s, 4H). $^{13}$C-NMR (100 MHz, CDCl$_3$, δ, ppm): 146.20, 140.62, 140.29, 140.10, 139.44, 136.20, 129.77, 129.41, 128.10, 127.61, 127.43, 127.00, 116.50, 116.05, 115.33, 114.83. HRMS (ESI) m/z: 427 [M + H]$^+$ Calcd. for C$_{33}$H$_{32}$N$_2$O$_7$: 487.2048. Anal. Calcd. for C$_{33}$H$_{32}$N$_2$O$_7$: C 84.28, H 5.89, N 9.83; Found: C 83.87, H 5.81, N 9.83.

Synthesis of TmBPPA film
A-TmBP (0.428 g, 1 mmol), pyromellitic dianhydride (PMDA) (0.218 g, 1 mmol), and purified DMF (4.3 mL) were added in a 50 mL flask to achieve a solid content of approximately 15 wt%. The mixture was stirred at room temperature under argon for about 4 h to form a viscous poly(amic acid) (PAA) solution. The PAA solution was subsequently coated uniformly on a clean and dry glass plate with a controlled film thickness, and then thermally imidized in a vacuum oven with the temperature program of 100 °C (1 h)/200 °C (1 h)/350 °C (1 h) to produce TmBPPA. The TmBPPA film was removed from the glass substrate after the oven was cooled to room temperature. IR (KBr, ν, cm$^{-1}$): 1778 (C=O stretching), 1500 (C=C stretching), 3032 (C≡H stretching), 1087−725 (Ar–H stretching), 1371 (C–N stretching). GPC (PAA in DMF) $M_n$: 5.68 × 10$^3$ g mol$^{-1}$, $M_w$: 8.67 × 10$^3$ g mol$^{-1}$, PDI: 1.52 (polystyrene standard). The intrinsic viscosity ($\eta$) of the PAA solution (0.5 g L$^{-1}$ in DMF) was 0.49.

RESULTS AND DISCUSSION
The new diamine monomer A-TmBP was synthesized according to Scheme 1. The precursor (PAA) was synthesized via A-TmBP and pyromellitic dianhydride (PMDA) in DMF for 24 h at room temperature. The intrinsic viscosity of the PAA solution (0.5 g L$^{-1}$ in DMF) is 0.49 dL g$^{-1}$. The final polymer TmBPPA film was prepared by thermal imidization.
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obtained by thermal imidization of PAA. TmBPPA exhibits good solubility in N-methyl/pyrrolidione (NMP), and as shown in Fig. 1(b), the TmBPPA film possesses good flexibility. Due to the high-\(k\) of water (\(k_{\text{water}} = 81\)), we measured the moisture absorption of the polymer film. The TmBPPA film exhibits moisture absorption of less than 0.78% after being soaked in deionized water at 25 °C for 24 h, which perfectly meets the requirement of ideal low-\(k\) materials. Such low moisture absorption is preferred for low-\(k\) materials and is attributed to the hydrophobic groups in the TmBPPA polymer chains. Scanning electron microscopy (SEM) image (Fig. 1d) shows that the film section is uniform and compact. Atomic force microscopy (AFM) image (Fig. 1d) shows that there are no apparent pores on the film surface, and the surface roughness (\(R_s\)) is 0.386 nm, which indicates the polyimide film contains no nanoporous structures after solution casting and subsequent solvent evaporation.

The \(k\) value of the TmBPPA film was measured by the capacitance method at various frequencies. The parallel plate capacitor was fabricated using Cu sheets (1 cm × 1 cm) as the electrodes sticking on the two surfaces of the TmBPPA film by silver paste (Fig. S1 in electronic supplementary information, ESI). The completed parallel plate capacitor underwent heat treatment at 120 °C for 2 h to remove the residual water and chemical solvents. All the capacitance data (\(C\)) was measured by an SI1260 impedance analyzer (Solartron, USA) in a constant temperature and humidity environment. The \(k\) value of the TmBPPA film was subsequently calculated from its capacitance (\(C\)) by Eq. (1):

\[
k = \frac{C d}{S k_0}
\]

(1)

where \(C\) is the obtained capacitance, \(d\) is the thickness of the TmBPPA film, \(S\) is the surface area of the Cu sheet electrode, and \(k_0\) is vacuum permittivity (8.854 × 10\(^{-12}\) F·m\(^{-1}\)). Fig. 2(a) shows the relationship of \(k\) and loss tangent with frequency in the range from 10\(^2\) Hz to 10\(^6\) Hz. The \(k\) values of the TmBPPA film kept below 2.3 and the loss tangent values of the TmBPPA film kept below 0.008 at these frequencies, which are much lower than those of other traditional intrinsic low-\(k\) non-fluorinated polymers (e.g., 2.25–2.35 for polyethylene, 2.45–3.10 for poly(styrene), and even some fluorinated polymers. More importantly, the \(k\) value of the TmBPPA film is extremely stable even when the temperature reaches 300 °C (Fig. 2b). There are two aspects that contribute to the reduction of \(k\) of the TmBPPA film. Firstly, the amorphous form of the TmBPPA molecular chains in the film, detected from wide angle X-ray diffraction (WAXD) (Fig. S2 in ESI), can effectively decrease orientation polarization and subsequently reduce the \(k\) value compared with a crystalline polymer. The second aspect is the additional free volume present in the polymer chains, which can greatly decrease the number density of the dipoles.

On the dynamic mechanical analysis (DMA) curve (Fig. 3), there is an obvious broad peak ranging from 50 °C to 200 °C that represents the \(\beta\) relaxation behavior of the polymer chains. For the TmBPPA film, the \(\beta\) relaxation behavior mainly corresponds to the rotation of side terphenyl unit connected to the nitrogen atom (blue unit of the structure inset in Fig. 3). The blue unit keeps a constant angle (60°) with the rotational axis, and the rotation of this side terphenyl unit connected to the nitrogen atom will create additional free volume like a cone. The additional free volume will not be influenced by the segment parking below \(T_g\) and can observably reduce the \(k\) value of the TmBPPA film.

To clearly verify the formation mechanism of additional free volume in the TmBPPA film, we synthesized two other polyimides (TPPA and TpBPPA) as references. As shown in Fig. 4(a), TPPA has the same polymer backbone structure as TmBPPA, but only contains a phenyl ring attached to the ni-
trogen atom as the pendant group, i.e., with no biphenyl unit attached to the meta-position of the phenyl ring. On the other hand, TpBPPA also has the same backbone structure as TmBPPA, but in this case, the phenyl ring is substituted with a biphenyl unit at the para-substitution. With regards to the chemical structure, the \( \beta \) relaxation behavior may occur in all these three polyimides (\( T_\beta^{TPPA} \): 139 °C, \( T_\beta^{TpBPPA} \): 145 °C, \( T_\beta^{TmBPPA} \): 150 °C, shown in Fig. S3 in ESI), but different molecular structures in the side-group will lead to different sizes of free volume created by the self-rotation of the side-group. In these three polyimides, only TmBPPA with meta-substitution shows more free volume by the rotation of its terphenyl unit in the pendant group. The increase in free volume can be verified by WAXD measurements and density testing compared to the TPPA film and the TpBPPA film. The WAXD peaks at 2\( \theta \) may be assigned to the interlayer distance of the polymer. The interlayer distance calculated from 2\( \theta \) data indicates that the TmBPPA film (\( d = 0.564 \) nm) has larger interlayer distance than the TPPA film (\( d = 0.541 \) nm) and the TpBPPA film (\( d = 0.524 \) nm) (see Fig. S2 and Table S3 in ESI). The density of the TmBPPA film (\( \rho = 1.2901 \pm 0.0030 \text{ g cm}^{-3} \)) and the TpBPPA film (\( \rho = 1.3263 \pm 0.0027 \text{ g cm}^{-3} \)) is higher compared with those of the TPPA film (\( \rho = 1.3263 \pm 0.0027 \text{ g cm}^{-3} \)) and the TpBPPA film (\( \rho = 1.2901 \pm 0.0030 \text{ g cm}^{-3} \)). The interlayer distance and density clearly demonstrate that the introduction of a biphenyl unit with meta-substitution in the side-group of the polymer chains (TmBPPA, \( \kappa = 2.23 \), tan\( \delta = 3.94 \times 10^{-3} \text{, 10 kHz} \)) can effectively increase the free volume due to the self-rotation of the terphenyl unit with meta-substitution in the side-group. The same tendency was found in the MD simulation of fractional free volume (FFV) (the details of MD simulation process are described in ESI). As shown in Table 1 and Fig. 5, the TmBPPA film has the largest FFV in these three polyimides, which also indicates the introduction of a biphenyl unit with meta-substitution as a side group to the polymer chains can effectively improve the free volume. Thanks to the more free volume, TmBPPA shows the lowest \( k \) value (2.23, 10 kHz) and tan\( \delta \) (3.94 \times 10^{-3}, 10 kHz) compared with TPPA (\( k = 3.48 \), tan\( \delta = 8.97 \times 10^{-3} \text{, 10 kHz} \)) and TpBPPA (\( k = 2.75 \), tan\( \delta = 5.31 \times 10^{-3} \text{, 10 kHz} \)) (Figs. 4b and 4c).

### Table 1 Simulated FFV of TPPA, TpBPPA, and TmBPPA.

| Sample   | FFV\(^{a}\) (H\(_2\)O, %) | FFV\(^{b}\) (O\(_2\), %) | \( k \) |
|----------|--------------------------|--------------------------|--------|
| TPPA     | 17.2                     | 11.4                     | 3.48   |
| TpBPPA   | 21.0                     | 15.6                     | 2.75   |
| TmBPPA   | 21.7                     | 16.5                     | 2.23   |

\(^{a}\) Simulated FFV based on a Connolly radius of 0.1325 nm; \(^{b}\) Simulated FFV based on a Connolly radius of 0.173 nm.

The thermostability of TmBPPA was evaluated by DMA (Fig. 3), thermal mechanical analysis (TMA) (Fig. S4 in ESI), and thermal gravimetric analysis (TGA) (Fig. S5 in ESI). The DMA results show that \( T_g \) of the TmBPPA film is about 352 °C. The TMA results show that the coefficient of thermal expansion (CTE) of the TmBPPA film is about 46 ppm K\(^{-1}\), and the TGA measurements show that the 5 wt% decomposition temperature for TmBPPA is 579 °C with a residual rate of 67% at
polymer (TmBPPA), which shows a new amorphous non-fluorinated and non-porous materials. In comparison with porous and fluorinated low-k materials, TmBPPA shows a higher modulus and bonding strength, which makes it more suitable for applications as flexible circuit materials with the characteristics needed for present and future high density, high speed, and high frequency electronic circuit designs for 5G wireless networks.

**CONCLUSIONS**

In summary, by full consideration of the secondary relaxation behaviors of the polymer macro-chains, we have designed and synthesized a new amorphous non-fluorinated and non-porous polymer (TmBPPA), which shows a $k$ value of 2.23 with a loss tangent of $3.94 \times 10^{-3}$ at $10^4$ Hz. Moreover, the TmBPPA film shows $k$ values below 2.30 in the range from $10^2$ Hz to $10^6$ Hz. Such $k$ value is lower than those of the previously reported low-$k$ non-fluorinated and non-porous polyimides. In comparison with porous and fluorinated low-k materials, TmBPPA shows a higher modulus and bonding strength, which makes it more suitable for applications as flexible circuit materials with the characteristics needed for present and future high density, high speed, and high frequency electronic circuit designs for 5G wireless networks.

**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/s10118-020-2339-4.

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