

Achieving Low Dielectric Properties through Increasing the Length of Phenyl Ring Pendant Group in Polyimides

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Abstract

Three polyimides (PPy6F, mBPPy6F and mTPPy6F) containing the same rigid polyimide main chain and different lengths of phenyl ring in pendant group were synthesized through a very easy method. The PPy6F, mBPPy6F and mTPPy6F films show an intrinsic k value of 2.92, 2.72 and 2.54, respectively, showing an obvious decreasing tendency and thus providing us a new but easy strategy to obtain low dielectric polymers. Meanwhile, the mTPPy6F shows excellent thermal stability, with a glass transition temperature (T_g) of 342 °C, 5wt% loss temperature of 551 °C, and a low moisture absorption of only 0.6 %. 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 process.

Key words polyimide, low dielectric, thermal stability, pendant group

Introduction

Low dielectric materials have been an urgent needing for many years owing to the fast developing of ultralarge-scale integration (ULSL) to higher integration and smaller dimension, which lead to crosstalk and capacitive coupling between the metal interconnect lines and thus increased signal delays^[1]. Several classes of dielectric materials have attracted scientific and industrial interest because of their excellent performance and huge potential as replacements for silicon oxide ($k = 3.9-4.3$).

Polyimides possess excellent thermal, mechanical, and dielectric properties and have been widely used for electronic packing and electrical insulation in microelectronics industries. Thus Polyimide is one of the most promising candidate materials for the next generation ILD (interlayer dielectric). However, the k -value of traditional polyimides is still unable to meet the requirement of low dielectric constant ($k < 2.5$), for example, the k value of commercial Kapton polyimide is typically 3.1-3.5. Hence, research on polyimides with low dielectric constant is of great significance.

In this contribution, we present a series of novel polyimides, which containing a same rigid polyimide main chain and different lengths of phenyl ring in pendant group. They were synthesized by polycondensation between novel diamines (PPy, mBPPy and mTPpy) and a common dianhydride (6FDA). Their chemical structures are shown in **Figure 1**. The PPy6F, mBPPy6F and mTPPy6F films show an intrinsic k value of 2.92, 2.72 and 2.54 respectively, showing an obvious decreasing tendency and thus providing us a new but easy strategy to obtain low dielectric polymers. Meanwhile, the mTPPy6F shows excellent thermal stability, with a glass transition temperature (T_g , by DMA) of 342 °C, 5wt% loss temperature of 551 °C, and a low moisture absorption of only 0.6 %. 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 process.

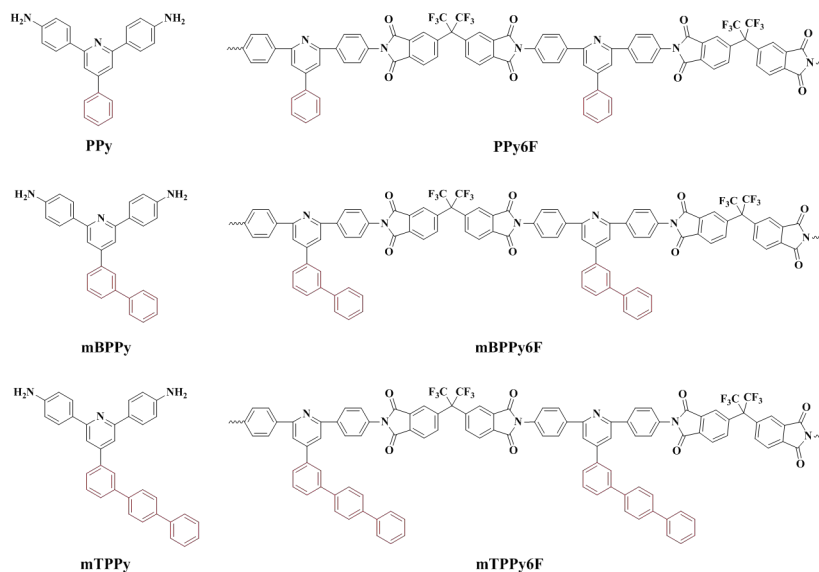


Figure 1. Chemical structure of the diamines (PPy, mBPPy and mTPPy) and their polyimides (PPy6F, mBPPy6F and mTPPy6F)

Results and discussion

Monomer synthesis

Three aromatic diamines (PPy, mBPPy, mTPPy) with different lengths of phenyl ring in pendant group were designed and successfully synthesized. Firstly, PPy was ‘one-pot’ synthesized according to the previous report^[2]. Then 3-bromobenzaldehyde was reacted with phenylboronic acid and 4-biphenylboronic acid respectively through Suzuki reaction with Pd[P(C₆H₅)₃]₄ as catalyst to produce BPhC and TPhC. Finally, the diamines mBPPy and mTPPy were obtained by the same reaction as PPy. The chemical structures of three diamines were confirmed by the ¹H NMR, ¹³C NMR spectra and the high resolution mass spectrum.

Polymer synthesis

The aromatic diamines were polymerized with 6FDA to produce the polyimides in a conventional two-step procedure. **Figure 2** shows the image of the as-prepared polyimide films.

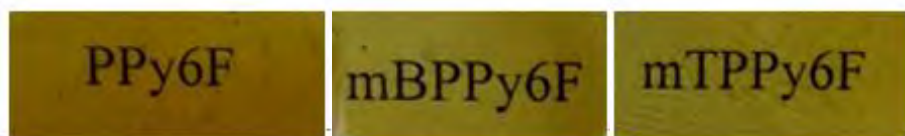


Figure 2. Images of the polyimide films produced by a solution casting process

Dielectric Properties of the Films.

The dielectric properties of the polyimide films were measured at the frequencies between 100 Hz to 1 MHz at 25 °C and 50% relative humidity using a Solartron SI 1260 impedance/gain phase analyzer (Solartron Group Ltd., U.K.). First, a capacitance measurement was carried out; then the dielectric constant of the polyimide films was calculated using eq (1):

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

Here, ε is the dielectric constant of the material between the plates, C is the capacitance of the material (in Farads), ε_0 is the electric constant ($\varepsilon_0 \approx 8.854 \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$), l is the thickness of the film (in meters), and A is the area of overlap of the two plates (in square meters). The results are shown in **Figure 3**.

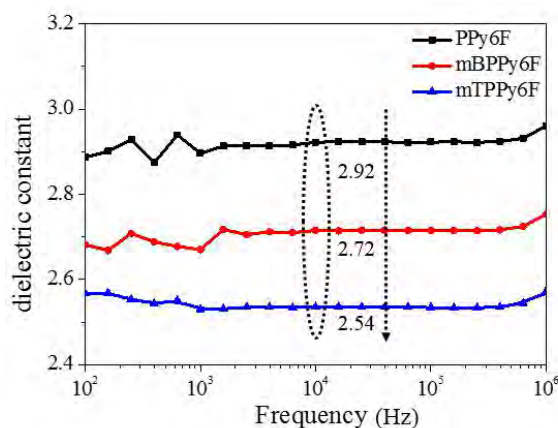


Figure 3. Dielectric properties of the pi films (PPy6F, mBPPy6F and mTPPy6F)

The k value of the PPy6F, mBPPy6F and mTPPy6F films is 2.92, 2.72 and 2.54 respectively (**Figure 3**), which shows an obvious decreasing tendency. The k values of the polyimide films decrease while the lengths of phenyl ring in pendant group increase. It is believable that the reduction in the k value of the films is attributed to larger free volume due to the incorporation of longer phenyl ring in pendant group. This could be proven by the density change of the polyimide films. As summarized in **Table 1**, mTPPy6F has the smallest density.

Table 1. Density Results of the polyimide films (PPy6F, mBPPy6F and mTPPy6F)

Polymers	PPy6F	mBPPy6F	mTPPy6F
Density / $\text{g}\cdot\text{cm}^{-3}$	1.3787	1.3513	1.3391
error	± 0.0013	± 0.0011	± 0.0022

In addition to the change of density, water absorption of the polyimide films also decreases while the lengths of the phenyl ring in pendant group increases. Water has a big influence to the dielectric properties of polymers because of its high dielectric constant ($k \approx 80$). Thus we guess the decrease of water absorption benefits from the hydrophobic property of phenyl ring and then help decrease the dielectric constant.

Table 2. Water absorption results of the polyimide films (PPy6F, mBPPy6F and mTPPy6F)

Polymers	Before water uptake (g)	After water uptake (g)	Water abs (wt%)
PPy6F	0.1472	0.1494	1.5
mBPPy6F	0.1695	0.1710	0.8
mTPPy6F	0.1592	0.1602	0.6

Other Properties of the Films

Because of the Pyridine ring in the polymer main chain, the polyimide films present an excellent thermal stability. As shown in **Figure 4**, both three polyimide films have a 5wt% loss temperature of about 550 °C. And the glass transition temperature (T_g) of PPy6F, mBPPy6F and mTPPy6F is 394 °C, 346 °C and 342 °C, respectively. In addition, the polyimides were soluble in many common polar solvents such as N-methylpyrrolidone (NMP), DMF, and dichloromethane (DCM). The enhanced solubility is attributed to the introduction of the polar group pyridine into the polymer. Such structure may increase the interactions between the polymer and the polar solvents. 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.

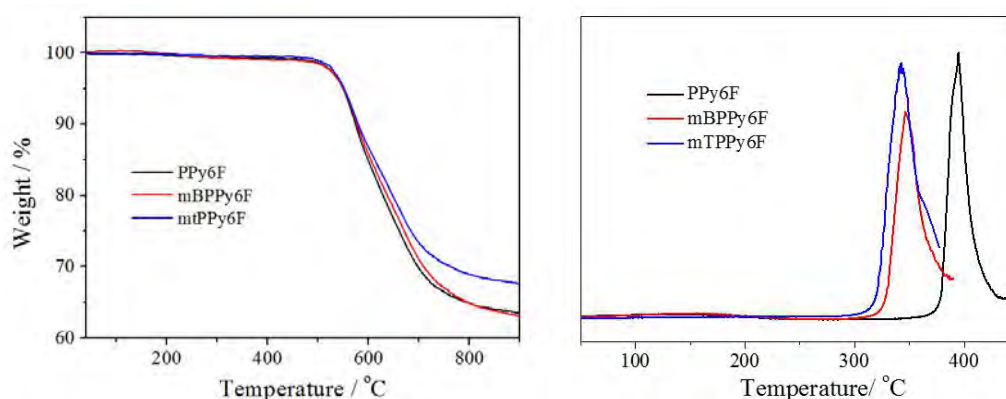


Figure 4. TGA curves and DMA thermograms of the pi films (PPy6F, mBPPy6F and mTPPy6F)

Table 3. Solubility of the polyimide films (PPy6F, mBPPy6F and mTPPy6F)

Polymers	NMP ^a	DMSO ^a	DMAc ^a	DMF ^a	CHCl ₃ ^b	DCM ^b	THF ^b
PPy6F	++	+-	+	++	+-	++	+-
mBPPy6F	++	+-	+	++	+-	++	+-
mTPPy6F	++	+-	+	++	++	++	+-

^a“++”, soluble at RT; “+”, soluble when heated at 90 °C; “+-”, partially soluble when heated at 90 °C;

^b“++”, soluble at RT; “+-”, partially soluble when heated at RT.

Conclusion

In summary, by increasing the length of phenyl ring in pendant group, we have obtained a series of novel polyimides with low- k and excellent comprehensive properties. 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.

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