polymers

MDPI

Article

Low Dielectric Polyimide Films for High Frequency Communication: Structure and Dielectric Properties

Yuwei Chen [1], Yidong Liu * and Yonggang Min *

[1] Guangdong University of Technology, No.100 Waihuanxi Road, Guangzhou HEMC, Guangdong, China (510006); polebear1996@outlook.com
[2] Guangdong University of Technology, No.100 Waihuanxi Road, Guangzhou HEMC, Guangdong, Chi-na (510006); zlla@foxmail.com
* Correspondence: zlla@foxmail.com, yong686@126.com

Abstract: Recent studies have shown that introducing fluorinated groups into the polyimide(PI) molecules can effectively reduce the dielectric constant(Dk) and dielectric loss(Df) of PIs. In this paper, 2,2′-bis [4-(4-aminophenoxy) phenyl]-1,1′,1′,3,3′,3′-hexafluoropropane (HFBAPP), 2,2'-bis(trifluoromethyl)-4,4'-diaminobenzene (TFMB), diaminobenzene ether (ODA), 1,2,4,5-Benzene-tetracarboxylic anhydride(PMDA), 3,3',4,4'-diphenyltetracarboxylic anhydride (s-BPDA) and 3,3',4,4' -diphenylketontetracarboxylic anhydride (BTDA) were selected for mixed polymerization to find the relationship between the structure of PIs and dielectric properties. Firstly, different structures of fluorinated PIs were determined, and were put into simulation calculation to obtain how structure factors such as fluorine content, the position of fluorine atom and the molecular structure of diamine monomer affect the dielectric properties. Secondly, experiments were carried out to characterize the properties of PI films. The observed change trends of performance were found to be consistent with the simulation results, and the possible basis of the interpretation of other performance was made from the molecular structure. Finally, the formulas with the best comprehensive performance were obtained respectively. Among them, the best dielectric properties was 14.3%TFMB/85.7%ODA//PMDA with dielectric constant of 2.12 and dielectric loss of 0.00698.

Keywords: fluorine; polyimide; dielectric properties; structural design

Citation: Chen, Y.; Liu, Y.; Min, Y. Low Dielectric Polyimide Films for High Frequency Communication: Structure and Dielectric Properties. *Polymers* **2023**, *14*, x. https://doi.org/10.3390/xxxxx

Academic Editor(s):

Received: date
Accepted: date
Published: date

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2023 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

With the development of science and technology, the requirements of mobile communication speed in various fields are becoming faster, and the concept of 5G communication arises at the historic moment of 3GPP designated 5G to support 450 MHz to 6 GHz and 24.25 to 52.6 GHz, which means that the communication wavelength has entered the era of millimeter wave [1]. Polyimide (PI) is favored by the electronics industry due to its excellent heat and corrosion resistance, electrical performance and processability, especially in the antenna group of communication receiving equipment [2-3]. When the insulating materials such as PI, were under the effect of electric field, energy loss always occurs due to their conductivity and the polarization of the hysteresis. In addition, energy loss also occurs when electromagnetic waves pass through the insulation, which affects the electro-magnetic wave signals, and the energy loss increases with the increase of wave frequency. When it comes to the millimeter wave band, the energy loss will be very significantly increased.

At present, the dielectric constant of commercial PI films on the market is above 3.0 (1 MHz), and the dielectric loss is above 0.01 (1 MHz)[4]. However, it can be predicted that when commercial PI films are applied to 5G or even higher frequency communication equipment, the energy loss will increase exponentially, indicting the commercial PI is hard to meet the demand in the near future[5]. In recent years, many research teams around

world have made non-negligible attempts to reduce the dielectric constant(Dk) and dielectric loss(Df) of polyimides[6]. Zeng[7] et al studied the factors affecting the dielectric properties of polyimide by molecular simulation. Qiu[8] et al prepared polyimide glass microspheres composite films and reduced the dielectric constant to 2.26-2.48 by changing the spatial structure of the polymer. And many other groups studied studied the effect of fluorine-containing groups on the dielectric properties of polyimide and prepared polyimide materials with dielectric constant below 2.5[9-15]. All of the researches above were consistant with the simulation result gained by Zeng, and the research datas show that the introduction of fluorine-containing groups is very beneficial to reducing the permittivity of polyimides. However, the modification can not be separated from the actual application demand, and other properties are ignored during the dielectric property modification.[16]

According to the relationship between the structure and properties of polymers, we find that the dielectric constant of polyimide is positively correlated with the polarizability, while the Df is related to the hygroscopicity. The higher the water absorption of the material, the greater the Df is [17-20]. The vitrification temperature is related to the pliability and interaction force of intermolecular chains[21-22], while the tensile strength is closely related to the chemical structure. By introducing the aromatic ring of the main chain, polarity of the side groups and hydrogen bonds could contribute synergetically to the increase of strength and chain rigidity[23-24]. The dense polar groups or substituents hinder the movement of chain segments, which can not achieve high elasticity but make the material more brittle[25]. Crosslinking can effectively enhance the connection between molecular chains and make them less prone to relative slip[26,27]. With the improvement of crosslinking degree, it is often less likely to occur large deformation and increase in strength[28]. As the degree of molecular chain branching increases, the distance between molecules increases, and the intermolecular force decreases, so the tensile strength decreases, but the impact strength increases [29].

Many attempts have been made to simulate the polymer polarizability. Ankit Mishra[l']s group[30] introduced reactive force field (ReaxFF) into the model simulation. ReaxFF force field uses the concept of bond level to structure the bond and non-bond (including van der Waals and Coulomb forces) between all atoms in the system[31]. Rinaldi et al.[32-33] made a detailed derivation of the calculation formula and boundary conditions of the polarization from the theoretical modeling. Rivail[34] went on to improve some of the formulas. While Bodo et al.[35] introduced the neglected differential diatomic overlap (NDDO) method into the previous theoretical derivation process and described the atomic charge calculation formula again.

In this study, 2,2′-bis [4-(4-aminophenoxy) phenyl]-1,1′,1′,1′,3,3′,3′-hexafluoropropane (HFBAPP) and 2,2'-bis (trifluoromethyl)-4,4'-diaminobenzene (TFMB) were selected as diaminobenzene monomer variab[illegible]diaminobenzene ether (ODA) as fixed diamine. 1,2,4,5-Benzenetetracarboxylic anhydride (PMDA), 3,3',4,4' -diphenyltetracarboxylic anhydride (s-BPDA), 3,3',4,4' -diphenylketontetracarboxylic anhydride (BTDA) were randomly copolymerized with diamines in ternary or quaternary composition. Firstly, the unit structure of PIs synthesized in this study was determined, and its model was imported into the software to calculate the polarizability, and the law of the polarizability changing with the structure was obtained through analysis. Then polymerization experiment was carried out to obtain the polyimide films by thermal imidization method, and mechanical properties, thermal properties, dielectric properties and hygroscopic properties was carried out . By comparing the simulation and characterization results, it was confirmed that Dk firstly increased and then decreased as the fluorine content increased, and BPDA was better than BTDA for the reduction of Dk and Df. Finally, the best polyimide film formulas were found by comparison. In HFBAPP group, the comprehensive properties of 50%HFBAPP/50%ODA//PMDA was the best, with tensile strength of 72 MPa, elongation at break of 17.32%, Tg of 351 °C, T5% of 540 °C, Dk of 2.39, Df of i 0.00702 and hygroscopicity of 0.917%. And in TFMB group, it was

14.3%TFMB/85.7%ODA//50%BPDA/50%PMDA, with tensile strength of 110 MPa, elongation at break of 20.23%, T5 of 568 °C, Dk of 2.12, Df of 0.00698 and hygroscopicity of 1.224.

The main contributions of this article are summarized in three aspects.

(1) This work uses a dual-line research path of simulation and actual experiment to study the related mechanisms and macro and micro performances of fluorine-containing groups affecting the dielectric properties of polyimide, and the theoretical and practical conclusions can be mutually verified.
(2) This work focuses on the high frequency use environment such as 5G communication, and specifically investigates the performance of the new polyimide films under the same frequency, temperature and humidity as the actual use environment.
(3) The polymerization schemes with excellent performance are concluded, which also provide a variety of directions for further industrial application research of the prepared films.

2. Simulation calculation

2.1. Model building

The molecular structures of PI that may be synthesized by ternary or quaternary polymerization in the experiments were determined, as shown in Fig. 1 and Fig.2. Then the molecular structures above were imported into the simulation software Material Studio 2019 (MS, Accelrys, America) to run the simulation.

Since the structures introduced in the simulation were the unit structures of each PI molecule, the volumes of the unit structure containing different amount of monomers were not equal, so only the structures with the same number of monomers were compared simultaneously. For the above reasons, we chose the single-chain structures of PIs in Fig.3 as the simulation models. And one of the models is shown in Fig.4, which is the model of PI polymerized by BPDA, ODA ad HFBAPP.

The module 'Forcite' was adopt to optimize the structure, and it was also used to relax the simulation system by firstly using NVT with steptime of 600ps under 298K. and then using NPT with steptime of 600ps under 298K and one standard atmosphere. Then we chose the module " CASTEP" and chose "polarizability"to calculate the molecular polarizability. And the electric field is set by MS software

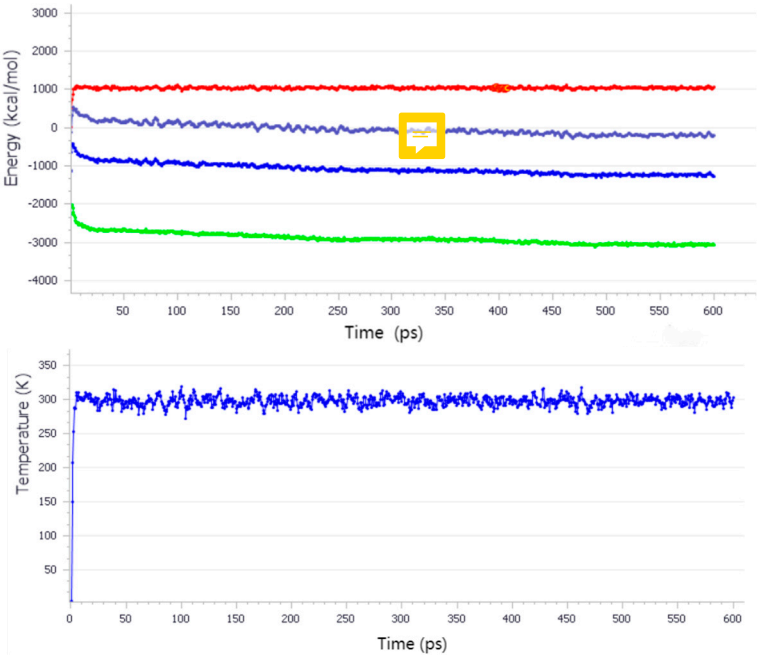


Figure 1. Dynamic energy and temperature curves of NVT ensemble.

It should be noted that under ideal conditions, all monomers labeled as participating in polymerization were polymerized in one main chain, and only the molecular structure of the main chain covering all monomers was calculated, without considering the difference caused by the number of short chains in polymerization and the ratio of monomers. The cross-linking and crystallization during polymerization and imidization were preset (the cross-linking could not be controlled, and crystallization was avoided as far as possible through experimental heating process and cooling process design).

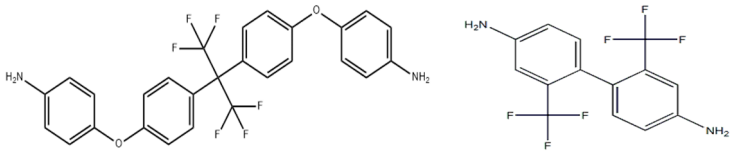


Figure 2. (a)Molecular structure of HFBAPP ;(b) Molecular structure of TFMB.

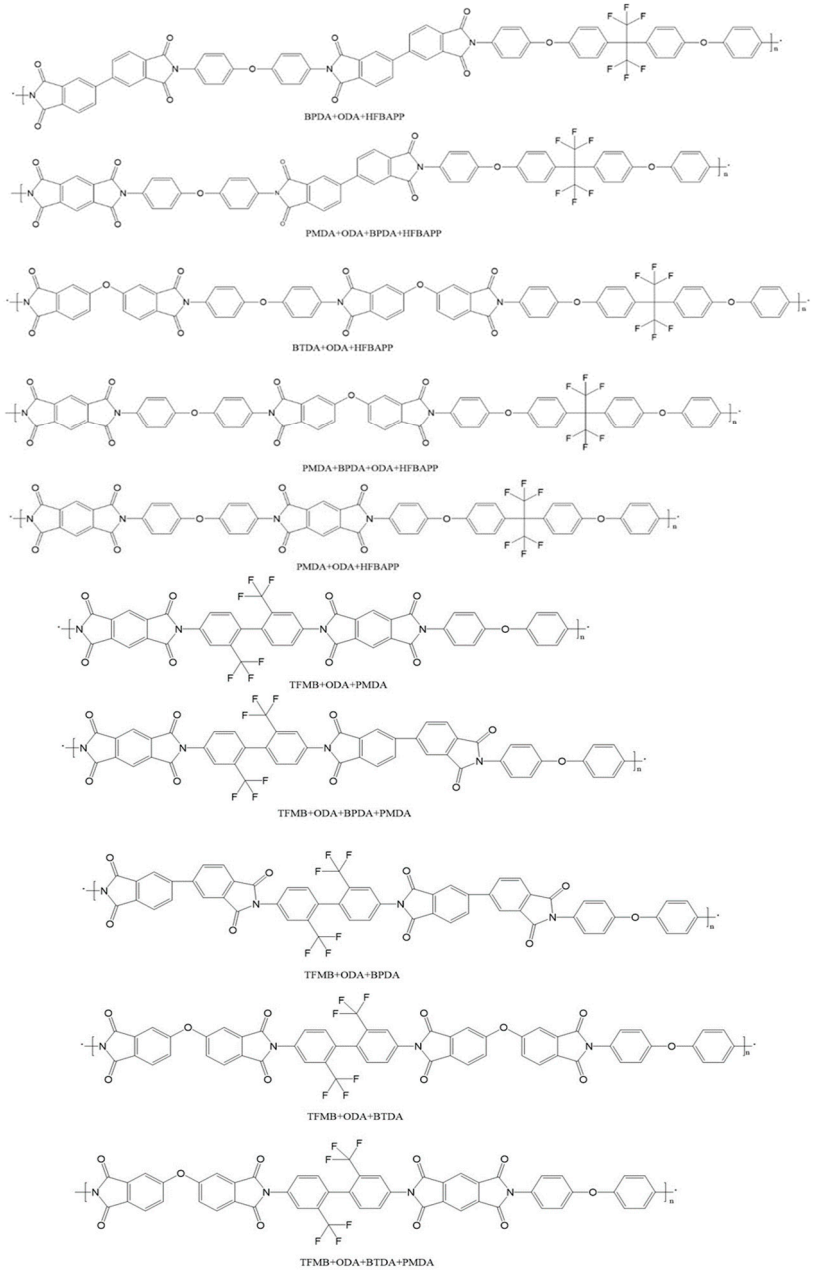


Figure 3. Molecular structure diagram of PIs of Group HFOB,HFOP,TFOB and TFOP.

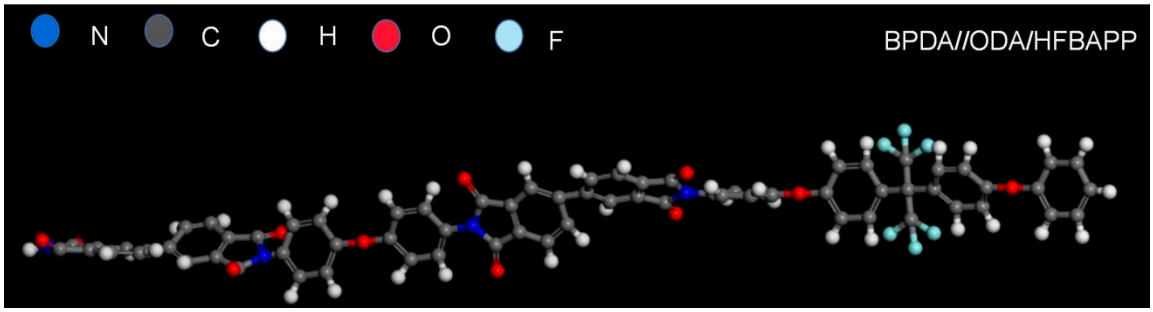


Figure 4. an example of models used for simulation: BPDA//ODA/HFBAPP.

2.2. Results of simulation

The final polarization results are shown in Table 1. It can be seen from the simulation results that the introduction of fluorinated groups greatly reduces the polarization of molecular structure, which confirms that the introduction of fluorinated groups is an effective means to reduce the dielectric constant and dielectric loss of PI materials. However, the datas of line 11/12/13 show that if ODA is completely re-placed with HFBAPP or TFMB, the polarization will increase . And HFBAPP has a larger polarization than TFMB due to its larger main chain structure than ODA and TFMB, indicating that when fluoride content is certain, the polarization will decrease negatively. For the ternary polymerization containing HFBAPP or TFMB, the polarization of PMDA is lower than that of BPDA and BTDA, and the Dk and Df of HFBAPP/ODA//PMDA and TFMB/ODA//PMDA will be lower. For the quaternion polymerization containing HFBAPP and TFMB, introducing BPDA and BTDA has little difference in the change of polarization, but introducing BPDA prefer to be relatively smaller, and both of them are smaller than ternary polymerization.

Table 1. Simulation results of the polarizability of PI films composed of each monomer group.

Monomers	Polarization result 1/ Angstrom3	Polarization result 2/cm³	Polarization result 3/a.u.
ODA/HFBAPP//PMDA	105.30900	1053.09001	710.66097
ODA/HFBAPP//BPDA	124.33796	1243.37963	839.07488
ODA/HFBAPP//BTDA	125.96996	1259.69965	850.08819
ODA/HFBAPP//BPDA/PMDA	114.35725	1143.57253	771.72166
ODA/HFBAPP//BTDA/PMDA	115.77274	1157.72736	781.27381
ODA/TFMB//PMDA	83.82904	838.29040	565.70689
ODA/TFMB//BPDA	102.40759	1024.07595	691.08130
ODA/TFMB//BTDA	103.66158	1036.61576	699.54359
ODA/TFMB//BPDA/PMDA	93.11482	931.14817	628.37047
ODA/TFMB//BTDA/PMDA	93.33594	933.35938	629.86267
ODA//PMDA	41.06345	410.63453	277.11015
HFBAPP//PMDA	65.68756	656.87561	443.28201
TFMB//PMDA	43.29990	432.99903	292.20248

3. Experiment

3.1. Reagents

HFBAPP was procured from Meryer, Shanghai China. And ODA (99%), PMDA (99%), DMAc, TFMB (98%), s-BPDA (98%), BTDA (98%) were obtained from Macklin, Shanghai China.

3.2. Ternary polymerization of different diamine and PMDA

First of all, HFBAPP and ODA were randomly copolymerized with PMDA in five molar ratios (pure HFBAPP, 3:1, 1:1, 1:3, pure ODA) at suitable stirring speed. The molar ratio of diamines to dianhydride was 1:1.01, the solid content was 20%, and the synthesis

conditions were room temperature and 30% humidity. A series of PAA pre-polycolloids were obtained, and then the PI films were recorded as group HFOP after thermal imidization at 100 °C, 200 °C and 300 °C. Then TFMB and ODA were randomly copolymerized with PMDA at a molar ratio of 1:4-1:10 at an appropriate stirring speed. The experimental conditions and procedures were the same as above. The finished PI membranes obtained was denoted as group TFOP.

3.3. Effects of different types of dianhydride

According to the experimental characterization results of the diamine group, we found that the molar ratios of the best performance were 1:1 in the group HFOP and 1:6 in the group TFOP. Therefore we chose these two proportions for the next experiment.

Group HFBAPP: The molar ratio of HFBAPP to ODA was 1:1, and then the terpolymer of HFBAPP was carried out with BPDA and BTDA respectively. The molar ratio of diamine to dianhydride was 1:1.01, the solid content was 20%, and the synthesis conditions were room temperature and 30% humidity. A series of PAA pre-polycolloids were obtained, and then thermal imidization method was used. After high temperature treatment at 100 °C, 200 °C and 300 °C, the PI films obtained were denoted as group HFOB1. Then, quaternary polymerization was performed with PMDA, BPDA and BTDA (the molar ratio of dianhydride was PMDA:BPDA=1:1, PMDA:BTDA=1:1). The experimental process was the same as above, and the finished PI membrane obtained was denoted as group HFOB2.

Group TFMB: The molar ratio of TFMB to ODA was 1:6, and then polymerized with BPDA and BTDA, respectively. The molar ratio of diamine to dianhydride was 1:1.01, the solid content was 20%, and the synthesis conditions were room temperature and 30% humidity. A series of PAA pre-polycolloids were obtained, and then the PI films were denoted as group TFOB1 after thermal imidization at 100 °C, 200 °C and 300 °C. Then, quaternal polymerization was performed with PMDA, BPDA and BTDA (the ratio of dianhydride was PMDA:BPDA=1:1, PMDA:BTDA=1:1). The experimental procedure was the same as above, and the finished PI membrane obtained was denoted as group TFOB2.

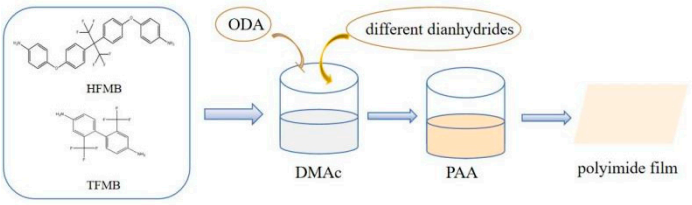


Figure 5. The synthesis process of fluorinated polyimides.

3.4. Measurements

The Fourier transform infrared (FTIR) spectra of PI films were obtained using a Nicolet 6700 Fourier Transform Infrared Spectrometer. Thermogravimetric analysis (TGA) of the polymer nano composites were carried out with an TGA 4000 (Holland) at a heating rate of 10 °C/min from 30 °C to 750 °C under N2 atmosphere. Differential scanning calorimetry (DSC) of the composites was tested by a DSC 8000 (Britain) at a heating rate of 20 °C/min from 30 °C to 450 °C under N2 atmosphere.

The dielectric constants and loss were determined by a Dielectric Spectrometer (Wuyi Electronic, Shanghai) in the range of 1 Hz to 1 MHz at 29% relative humidity. All of the films were cut into squares with the side length of 50mm and the thickness of 25-30μm. The capacitance, dielectric loss and thickness of the film were obtained directly during measurement, and then the dielectric constant was calculated by the equation 1.(The results of the calculation were reserved for two decimal places.)

$$\varepsilon_r = \frac{C \cdot d}{\varepsilon_0 \cdot S} \quad (1)$$

In which C is the value of capacitance, d is the thickness of films, ε_0 is vacuum dielectric coefficient, ε_r is the relative dielectric constant, and S is the measured area of the film.

The hygroscopicity of PI films was measured according to GB/T1033-1998.The details were as follows.

The PI films were cut into square pieces with the size of 5cm x5cm and dried in a 60-degree oven for 24h. The mass m_1 was then weighed. Then it was soaked in deionized water for 24h, and weighed immediately after wiping the water on the surface of the film to obtain the mass m_2. Each sample was measured three times and averaged. The hygroscopicity can be obtained by the following formula.

$$(m_2 - m_1)/m_1 \times 100\% \quad (2)$$

4. Result

4.1. Structural elucidation: FTIR

According to the infrared spectrogram shown in Fig.5, four absorption peaks are observed at 716 cm-1, 1370 cm-1, 1716 cm-1 and 1780 cm-1, corresponding to bending vibration peak of C=O, stretching vibration peak of C-N and stretching vibration peaks of C=O respectively, which proved the completion of imidization. In addition, absorption peaks of C-F bond are observed at 1173 cm^{-1}, 1213 cm^{-1} and 1247 cm^{-1}, indicating that -CF_3 structure has been successfully introduced into PI molecule structure. According to the data above, it can be found that fluorine-containing groups can be perfectly introduced into the main chain structure of polyimide without affecting the normal formation of the imide group.

4.2. Thermal properties

Data in Table 2 showed that there was no direct linear relationship between Tg and T5% and fluoride content in the HFOP group. However, after HFBAPP was added, the glass transition temperature increased, while T5% decreased. Fall all this, however, Tg were still above 320 °C and T5% were still above 490 °C, which meet the processing and use requirements of 5G antenna substrate. What's more, the Tg of HFBAPP:ODA=1:1 was more than 350 °C, and the T5% was 540 °C, showing excellent thermal performance. The thermal performance data of different compositions of dianhydride in Table 2 showed that the incorporation of BPDA could retain the excellent thermal performance of HFOP group to a greater extent. Although Tg decreased, it maintained at about 300 °C , and T5% was 540 °C at the same time, which met the needs in some industrial situations.

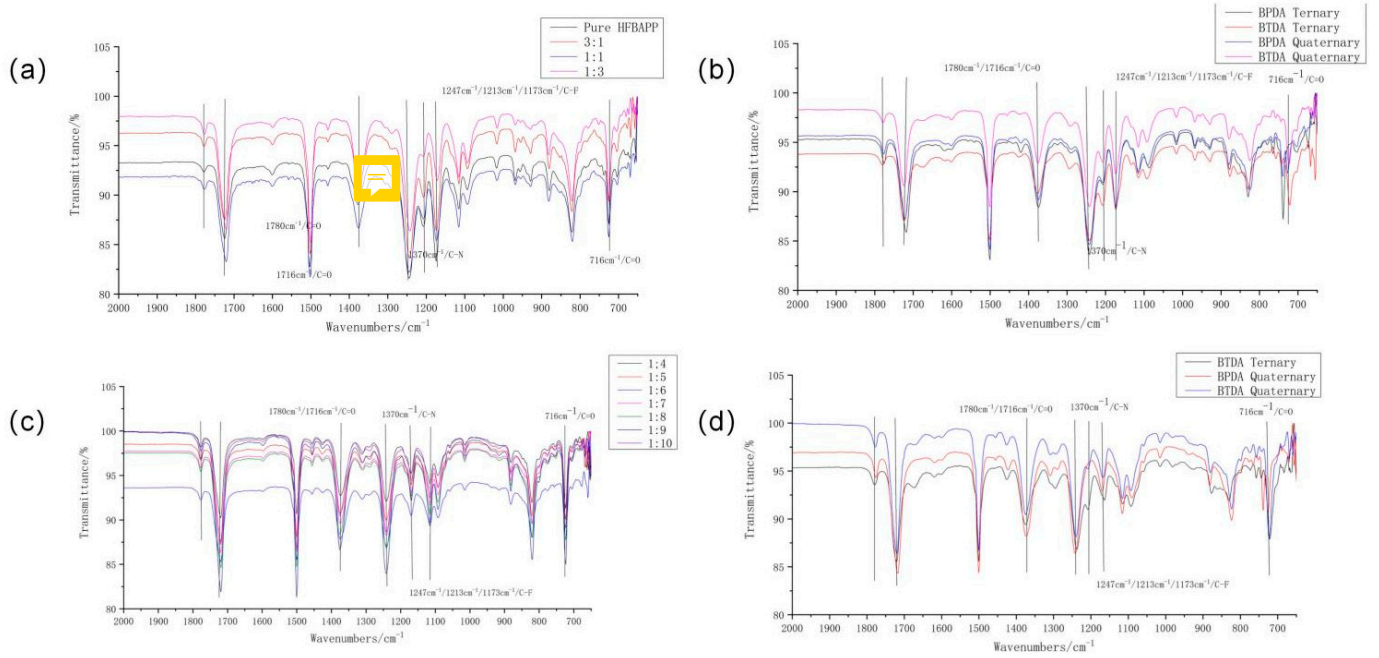


Figure 5. FTIR spectra of fluorinated PI films (a) FTIR spectra of group HFOP;(b) FTIR spectra of group HFOB;(c) FTIR spectra of group TFOP;(d) FTIR spectra of group TFOB.

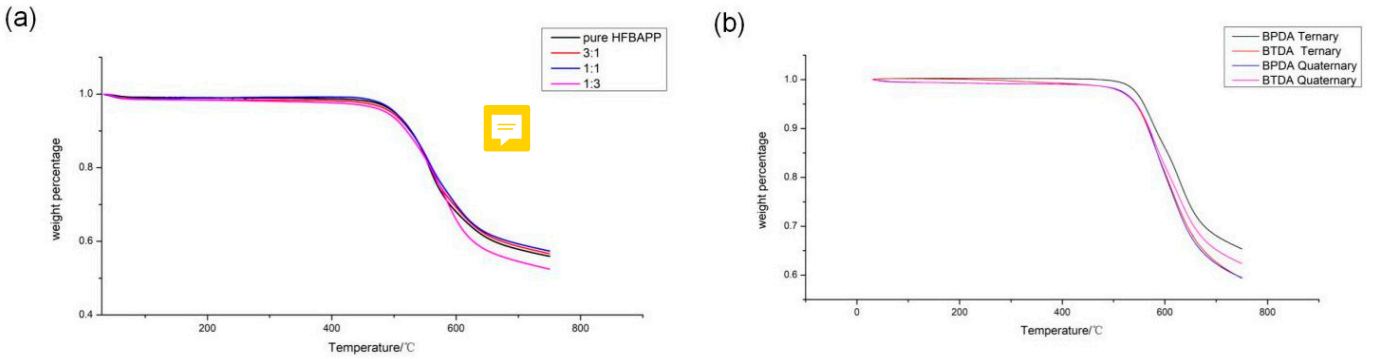


Figure 6. Thermal properties of Group HFOP and HFOB. (a) TGA curves of group HFOP (b) TGA curves of group HFOB.

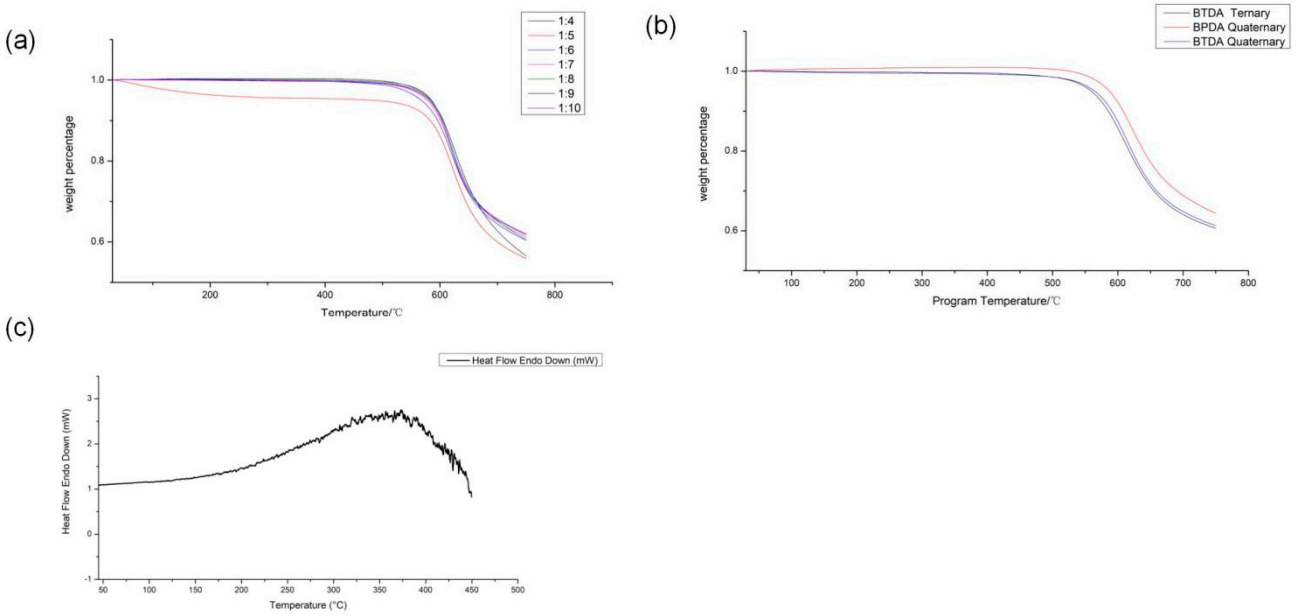


Figure 7. thermal performance diagram of group TFOP and group TFOB.(a) TGA curves of group TFOP (b) TGA curves of group TFOB (c) DSC curve of PI film when TFMB:ODA=1:6.

Table 2. Thermal properties of PI films in group HFOP and group HFOB.

Monomers	T_g/°C	$T_{5\%}$/°C
ODA//PMDA	340	550
25%HFBAPP/75%ODA//PMDA	346	490
50%HFBAPP/50%ODA//PMDA	351	540
75%HFBAPP/25%ODA//PMDA	321	500
HFBAPP//PMDA	320	510
50%HFBAPP/50%ODA//BPDA	278	560
50%HFBAPP/50%ODA//BTDA	275	543
50%HFBAPP/50%ODA//50%BPDA/50%PMDA	297	540

Table 3 showed that the thermal properties of PI films in TFOP and TFOB groups were excellent, and the T5% of PI films kept above 560°C regardless of the changes of fluoride content and monomer components. However, this kind of film has the problem that the glass state transition was not obvious. In the DSC test, even when the heating rate was raised to 20K/min, no obvious glass transition interval could be observed (as shown in the Fig.7). According to the structure of TFMB and dianhydride, we preliminary judged that it was probably because crosslinking produced in the polymerization. And high degree of crosslinking, to a certain extent, hampered the movement of molecular chain under high temperature, characterized as high thermo-gravimetric temperature, while hindered the PI films on the macro shift from glass state to the high elastic state, which made the change interval not obvious, or interval temperature so high as no obvious Tg point was observed in the conventional Tg interval.

From the data in Table 3, it can be seen that in the TFMB group, the T5% of PI film of TFMB:ODA=1:6 is 568°C, and the T5% of TFMB:ODA=1:6/BPDA:PMDA=1:1 is 587°C. These are both excellent thermal performance, and make the new PI suitable for many high temperature applications. In conclusion, from the perspective of thermal performance, adding an appropriate amount (25%-50%) of HFBAPP appropriately increased the glass transition temperature of PI film. And adding TFMB increased the temperature of 5% weight loss. However, the drawback was that the Tg point was not obvious, so the two could be selected and proportioned according to the direction of demand.

It is confirmed that the introduction of fluorine-containing groups can indeed have a positive effect on the thermal stability of polyimide. However, according to polymer physics, the thermal stability of polymer is related to bond energy and crosslinking degree. The C-F bond has a relatively high bond energy, and the fluorinated diamines selected in this experiment all have three C-F bonds, which undoubtedly has a significant impact on the thermal stability. However, From the data in Table 2 and 3, they don't show an obvious linear relationship. It is speculated that this may be caused by the failure to control the molecular weight, main chain length and mass ratio of short chain, so that the macro thermal stability of each component is affected by many structural factors, and the influence mechanism is complex, and finally the difference in data is presented.

Table 3. Thermal properties of PI films in group TFOP and group TFOB.

	Monomers	$T_{1\%}$/°C	$T_{5\%}$/°C
TFMB:ODA	1:4	531	582
	1:5	502	581
	1:6	488	568
	1:7	507	575
	1:8	533	585
	1:9	511	581
	1:10	519	583
TFOB	14.3%TFMB/85.7%ODA//BTDA	472	560
	14.3%TFMB/85.7%ODA//50%BPDA/50%PMDA	550	587
	14.3%TFMB/85.7%ODA//50%BTDA/50%PMDA	456	567

4.3. Mechanical properties

It can be seen from the data in Table 4 that there was no mathematical relationship between the fluoride content and the tensile strength and elongation at break of PI films, but it can be seen that the introduction of HFBAPP could indeed strengthen the mechanical properties of PI films at certain proportion points. Especially for 25%HFBAPP/75%ODA//PMDA and 50%HFBAPP/50%ODA//PMDA, the tensile strength of PI films was increased to 73 MPa and 72 MPa respectively, and the elongation at break were increased to 18.22% and 17.32%. The flexibility of PI film was greatly improved. According to the polymer physics, the tensile strength of the polymer materials depends on the chemical bond force of the main chain and the intermolecular force. The introduction of HFBAPP made the molar ratio of aromatic heterocyclic in the unit structure of the modified PI material increase, which was reflected in the macroscopic improvement of the tensile strength and elongation at break of the modified PI films. However, when the proportion of HFBAPP increased, the effect of reduced polarizability on mechanical properties began to exceed that of aromatic hetero ring, and both tensile strength and elongation at break began to decrease.

Table 4. Mechanical properties of PI films in group HFOP and group HFOB.

Monomers	Tensile strength /MPa	elongation at break /%
ODA//PMDA	54.	8.289
25%HFBAPP/75%ODA//PMDA	73	18.22
50%HFBAPP/50%ODA//PMDA	72	17.32
75%HFBAPP/25%ODA//PMDA	48	11.74
HFBAPP//PMDA	50	11.05
50%HFBAPP/50%ODA//BPDA	66	10.59
50%HFBAPP/50%ODA//BTDA	65	12.82
50%HFBAPP/50%ODA//50%BPDA/50%PMDA	62	12.23

In group TFOB, the PI films of BPDA ternary polymerization have become wrinkled and fragile after imidization at 350 °C, indicating that the molecular bonds inside have begun to break, which means that the thermal properties of the PI films of this formula cannot meet the requirements, so no performance test is conducted on it.

Due to the strong molecular structure rigidity of TFMB, it can be predicted that when the proportion of TFMB in the diamine system increases, the tensile strength will increase, and will begin to decline to a certain critical point. At this time, the PI film will be very brittle, and the elongation at break will decrease accordingly. Due to the pre-experiment, we found that when the ratio of TFMB and ODA was greater than 1:4, the PI films were relatively brittle. When the ratio was 1:4, there was no fracture of PI films after multiple folds. We judged that the mechanical properties of PI films within this ratio could be incorporated into further experimental plans.

As can be seen from Table 5, the tensile strength showed a trend of first increasing and then decreasing, while the elongation at break showed no obvious linear trend. As the tensile strength is closely related to molecular chemistry, there are many influencing fac-tors. We speculated its rise because of the side chain - CF_3 to strong polar bond, which drastically reduced the polarity of the molecular structure of the material. At the same time, although dense TFMB substituents made PI films brittle, the influence weakened as the reduce of TFMB. When the ratio of TFMB:ODA was among 1:4 to 1:6, the positive effect on tensile strength covered the negative influence of the latter. Then, as the content of TFMB in the diamine system continues decreased, the proportion of side chain decreases, and the positive influence of tensile strength weakens, so the tensile strength begins to de-cline. In group TFOP, the best ratio of tensile strength was TFMB:ODA=1.6, the tensile strength was 110 MPa, and the optimal ratio of elongation at break was TFMB:ODA=1:4, and the elongation at break reached 23.15%.

Table 5. Mechanical properties of PI films in group TFOP and group TFOB.

	Monomers	Tensile strength /MPa	elongation at break /%
TFMB:ODA	1:4	92	23.75
	1:5	106	18.72
	1:6	110	20.23
	1:7	89	19.88
	1:8	80	21.84
	1:9	54	10.88
	1:10	59	15.29
TFOB	14.3%TFMB/85.7%ODA//BTDA	56	9.23
	14.3%TFMB/85.7%ODA//50%BPDA/50%PMDA	56	9.23

The data in Table 5 above also showed that when PMDA was changed into BPDA or BTDA, the mechanical properties of PI material decline significantly. We speculated that the reason was the same as HFBAPP group, and since the molar mass of TFMB itself was much smaller than that of HFBAPP, when the average molar mass of PI increases, TFMB structure had a weaker effect on mechanical properties than HFBAPP. Similar to HFBAPP group, further change of the ratio of dianhydride did not have much effect on the mechanical properties of the material, and the tensile strength and elongation at break had no significant change and obvious trend. In the TFOB group, the best ratio of mechanical properties was 14.3%TFMB/85.7%ODA//50%BPDA/50%PMDA, at which the tensile strength was 56 MPa and the elongation at break was 9.23%.

4.4. Dielectric properties and hygroscopic

As could be seen from Table 6, both dielectric constant and dielectric loss decreased as the proportion of HFBAPP in the diamine system increased, which was consistent with the relationship of fluorine content in PI unit structure and dielectric constant and dielectric loss in the simulation calculation. However, the hygroscopicity didn't show a linear relationship, but decreased first and then increased. The hygroscopicity of fluorine PI films was within 1.5%. Water absorption of materials is related to hydrophilicity, hydrophobicity, porosity and pore size. The PI films prepared in this experiment did not have any pore-forming treatment, and the incorporation of air was also avoided in the preparation, and they were all hydrophobic films. The addition of fluorine atom enhanced the electronegativity of PI molecular structure, weakened the polarity, and further reduced the water absorption rate of PI films. However, there was no linear relationship between water absorption rate and fluoride content. We conjectured that when fluoride content increased to a certain extent, the influence on PI unit molecular structure was greater than the gain brought by electronegativity, leading to a certain increase in water absorption rate. According to the three data, when the ratio of HFBAPP:ODA was 1:1, the dielectric constant was 2.39, dielectric loss was 0.00702, and hygroscopicity was 0.917%

Table 6. Dielectric properties and hygroscopic of PI films in group HFOP and group HFOB.

Monomers	Dk（1MHz）	Df（1MHz）	Moisture absorption rate（%）
ODA//PMDA	3.03	0.0115	2.778
25%HFBAPP/75%ODA//PMDA	2.53	0.00753	1.575
50%HFBAPP/50%ODA//PMDA	2.39	0.00702	0.917
75%HFBAPP/25%ODA//PMDA	2.29	0.00645	1.034
HFBAPP//PMDA	2.21	0.00612	1.213
50%HFBAPP/50%ODA//BPDA	2.38	0.00734	1.525
50%HFBAPP/50%ODA//BTDA	2.37	0.00813	1.727
50%HFBAPP/50%ODA//50%BPDA/50%PMDA	2.40	0.00730	1.000
50%HFBAPP/50%ODA//50%BTDA/50%PMDA	2.41	0.00801	1.052

The data in Table 6 also showed that the dielectric properties and hygroscopicity of PI films obtained by ternary tetrad polymerization involving BPDA and BTDA were not different from each other. The performance of BPDA group was slightly better than that of BTDA group, but both were slightly worse than HFBAPP:ODA=1:1 in Table 6, which was consistent with the polarization change result obtained by simulation calculation. The optimal ratio of dielectric properties was 50%HFBAPP/50%ODA//BPDA, with dielectric constant of 2.38 and dielectric loss of 0.00734. The optimal ratio of hygroscopicity was 50%HFBAPP/50%ODA//50%BPDA/50%PMDA, and the hygroscopicity was only 1%.

Table 7. Dielectric properties and hygroscopic of PI films in group TFOP and group TFOB.

	Monomers	Dk (1MHz)	Df (1MHz)	Moisture absorption rate (%)
TFMB:ODA	1:4	2.08	0.00743	1.901
	1:5	2.10	0.00715	1.569
	1:6	2.12	0.00698	1.224
	1:7	2.24	0.00756	1.504
	1:8	2.44	0.00794	1.757
	1:9	2.53	0.00815	1.825
	1:10	2.65	0.00873	2.158
TFOB	14.3%TFMB/85.7%ODA//BTDA	2.19	0.00745	1.458
	14.3%TFMB/85.7%ODA//50%BPDA/50%PMDA	2.29	0.00786	1.274
	14.3%TFMB/85.7%ODA//50%BTDA/50%PMDA	2.25	0.00762	1.128

Due to the pre-experiment, we found that the ratio of diamine in the HFOP group was not suitable for the TFOP group. When TFMB:ODA was 1:3, the synthesized PI films were very brittle. After the high temperature of 350 °C, the surface of PI films had obvious folds, which meant that the molecular structure broke at the beginning. Therefore, the TFOP group was tested from 1:4. As can be seen from the table 7, the dielectric constant and dielectric loss of TFOP group decreased with the increase of TFMB in the diamine system, reaching the lowest of 2.08(TFMB:ODA=1:4) and 0.00682(TFMB:ODA=1:6) respectively. It could be conjectured that the dielectric performance was very ideal. Meanwhile, although the hygroscopicity first decreased and then increased, there was no obvious linear relationship. The lowest hygroscopicity of PI film in TFOP group was 1.224% (TFMB:ODA=1:6).This was because when the diamine mole ratio started from 1:4, the fluoride content in PI perfectly avoided the inverse influence interval, which made the polarization decrease with the in-crease of fluoride content. Meanwhile, because the CF3 bond of TFMB was directly connected to the benzene ring, the molar mass of TFMB was smaller, and the fluoride content of TFMB was higher than that of HFBAPP and TFMB with the same molar amount. Be-sides, TFMB had an asymmetric structure, which reduced polarity to a higher degree than HFBAPP, so it had a better improvement in dielectric performance.

In Table 7, when the ratio was 14.3%TFMB/85.7%ODA//PMDA, PI films had the best dielectric performance. At 1 MHz, the dielectric constant was 2.12, the dielectric loss was 0.00732, and the moisture absorption rate was 1.224%. Then the ratio of dianhydride was replaced, we found that, the dielectric properties of BTDA and TFMB were better than that of BPDA, which showed a little difference with the simulation calculation result. This was because in the simulation, the effect of crosslinking on the polarization did not be considered, and TFMB and dianhydride aggregation might crosslinking. So we inferred that when TFMB polymerized with BTDA, crosslinking occurred, contributing to the result of dielectric properties of PI films prepared by polymerization with BPDA better than those prepared by polymerization with BTDA. And in the TFOB group, the best ratio of dielectric performance was 14.3%TFMB/85.7%ODA//50%BTDA/50%PMDA. At this time, the dielectric constant of PI films was 2.25, and the dielectric loss was 0.00762, meanwhile moisture absorption rate was 1.128%.

In conclusion, in terms of dielectric properties, TFMB can reduce the dielectric constant of PI film more than HFBAPP, while HFBAPP is more suitable for introducing modified molecular structure than TFMB for hygroscopicity and dielectric loss.

5. Conclusions

In this study, three kinds of diamines (including two kinds of fluorinated diamines with different structures) and three kinds of dianhydride were selected to characterize the

performance of PI films polymerized by them through simulation calculation and experiment. Since only the polarization of the structure is considered in the simulation calculation, and the factor is relatively single, the simulated change trend of the performance is slightly different from the experimental results, but generally consistent, and the difference can also be inferred according to the structure. The results show that the formula with the best comprehensive performance in HFBAPP group is 50%HFBAPP/50%ODA//PMDA. At this time, the tensile strength of PI film is 72MPa, elongation at break is 17.32%, Tg is 351°C, T5% is 540°C, dielectric constant is 2.39, dielectric loss is 0.00702.Hygroscopicity is 0.917%.The formulas with better comprehensive performance in TFMB group are 14.3%TFMB/85.7%ODA//PMDA and 14.3%TFMB/85.7%ODA//50%BPDA/50%PMDA.The tensile strength of PI film is 110MPa, elongation at break is 20.23%, T5% is 568°C, dielec-tric constant is 2.12, dielectric loss is 0.00698, and hygroscopicity is 1.224.The latter PI film has tensile strength of 56MPa, elongation at break of 9.234%, T5% of 587°C, dielectric con-stant of 2.29, dielectric loss of 0.00786, and hygroscopicity of 1.274.In actual production, formulations with better performance can be selected for further experiments according to the target performance

Author Contributions: Conceptualization, Yuwei Chen and Yidong Liu.; methodology, Yuwei Chen.; software, Yuwei Chen.; validation, Yuwei Chen, Yidong Liu and Yonggang Min.; formal analysis, Yuwei Chen.; investigation, Yuwei Chen.; resources, Yuwei Chen.; data curation, Yuwei Chen; writing—original draft preparation, Yuwei Chen.; writing—review and editing, Yuwei Chen.; project administration, Yidong Liu.; funding acquisition, Yonggang Min. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by National Key R&D Program of China (2020YFB0408100), NSFC (U20A20340), the Program for Guangdong Introducing Innovative and Entrepreneurial Team (2016ZT06C412), Foshan Introducing Innovative and Entrepreneurial Teams (No. 1920001000108), the Hundred Talent Program of Guangdong University of Technology (220418095). We want to thank Dr. Tingting Cui for assisting in simulation calculations.

Data Availability Statement: In this section, please provide details regarding where data supporting reported results can be found, including links to publicly archived datasets analyzed or generated during the study. Please refer to suggested Data Availability Statements in section "MDPI Research Data Policies" at https://www.mdpi.com/ethics. You might choose to exclude this statement if the study did not report any data.

Acknowledgments: We acknowledge PhD. Cui for providing simulating assistance.

References

1. BOC INTERNATIONAL(CHINA). 5G series: Special topics on terminal Antenna. Electronic Securities Research Re-port. 2019, 2。
2. Christopher D, Simonea, Eleonora Vaccaro, et al. The Synthesis and Characterization of Highly Fluorinated Aromatic Polyimides[J]. Journal of Fluorine Chemistry. 2019, 224, 100-112.
3. LI X T. Synthesis and properties of phenylacetylene terminated polyimide resin with low dielectric constant [D]. Donghua University. 2021.
4. HUANG Fu, MENG Ge, GUO Yidan, ZHI Xin-xin, ZHANG Yan, WU Lin, JIA Yan-jiang, LIU Jing-gang. Research and development of low dielectric polymer materials under the background of 5G demand [A]. China Electronic Material Industry Association Copper Clad Material Branch, China Electronic Circuit Industry Association copper clad material branch. Proceedings of the 21st China Copper Clad Panel Technology Seminar [C]. Copper Clad Panel Material Branch of China Electronic Materials Industry Association, Copper clad Panel Branch of China Electronic Circuit Industry Association: Copper clad Panel Material Branch of China Electronic Materials Industry Association, 2020, 8.
5. Yang Zhenghui, GUO Haiquan, GAO Lianxun. Structure design and high frequency dielectric properties of polyimide [A]. Copper Clad Material Branch of China Electronic Materials Industry Association, Copper clad Panel Branch of China Electronic Circuit Industry Association. Proceedings of the 21st China Copper Clad Panel Technology Seminar [C]. Copper Clad Panel Material Branch of China Electronic Materials Industry Association, Copper clad Panel Branch of China Electronic Circuit Industry Association: Copper clad Panel Material Branch of China Electronic Materials Industry Association,2020:5.
6. Wang Hai, Cheng Wenhai, Zhou Taotao, Lu Zhencheng, Wang Lingzhen, Jiang Liangshu. Research progress of organic materials containing fluorine with low dielectric constant [J]. Organic Fluorine Industry. 2020, 02, 30-34.

7. Zhen-guo Fan, Wen-xin Chen, Shi-yang Wei. Quantitative Structure-Property Relationship Study on Dielectric Constant of Polyimide and Its Molecular Structure Design for Low Dielectric Films[J]. ACTA POLYMERICA SINICA. 2019, 50(2), 179-188.
8. Guorong Qiu, Wenshi Ma, Li Wu. Low dielectric constant polyimide mixtures fabricated by polyimide matrix and polyimide microsphere fillers[J]. Polymer International. 2020, 5(69), 485-491.
9. Chen-yi Wanga, Wen-tao Chena, Chang Xua. Fluorinated Polyimide/POSS Hybrid Polymers with High Solubility and Low Dielectric Constant[J]. Chinese Journal of Polymer Science. 2016, 34(11), 1363-1372.
10. Henxun Huang, Jianqing Zhao. Low-k and superior comprehensive property hybrid materials of a fluorinated polyi-mide and pure silica zeolite[J]. RSC Advances. 2016, 6, 1-8.
11. Li X J. Preparation and properties of fluorinated copolymer polyimide films [D]. North University of China, 2021.
12. Ziqi Wang; Mengying Zhang; Enlin Han; Hongqing Niu; Dezhen Wu. Structure-property relationship of low dielectric constant polyimide fibers containing fluorine groups[J]. Polymer. 2020, 206.
13. Revathi Purushothaman, Hari Shankar Vaitinadin. Inclusion of covalent triazine framework into fluorinated polyimides to obtain composites with low dielectric constant[J]. Journal of Applied Polymer Science. 2020, 37(137).
14. Ting Zhang, Yang Pan; Cheng Song, Bin Huang, Zhen-Zhong Huan. High optical transparency, low dielectric constant and light color of organosoluble fluorinated polyimides based on 10,10-bis[4-(4-amino-3-tri-fluoro-methylphenoxy)phenyl]-9(10H)-anthrone [J].Polymer Bulletin. 2019, 1-18.
15. Saritha B, Thiruvasagam P. Synthesis of diol monomers and organosoluble fluorinated polyimides with low dielectric[J]. High Performance Polymers. 2015, 7(27), 842-851
16. Mousa Ghaemy, Farshad Rahimi Berenjestanaki, Maasoomeh Bazzar. Organosoluble, thermally stable and low dielectric constant fluorinated polyimides containing 2,4,5-triphenylimidazole moiety in the main chains[J]. Designed Monomers and Polymers. 2014, 2(17), 101-110.
17. Fei Chen, Debaditya Bera, Susanta Banerjee, Seema Agarwal. Low dielectric constant polyimide nanomats by electrospinning[J]. Polymers for Advanced Technologies. 2012, 6(23), 951-957
18. Li Bin, Xia Yao, An Hongli, Jiang Shuang, Zhang Tianyong. Design, synthesis and application of fluorinated polyimides [J]. Fine Chemicals. 2018, 38(07), 1314-1324.
19. Ma D P, Tao K K, Wang C W, et al. Structural design and performance research of low-dielectric polyimide composite sheet[J]. Plastics Science and Technology. 2022, 50(6), 74-78.
20. Yongjian Li, Zhongkai Wang, Tangsong Zhu, Haixia Qi, Lei Xiong, Feng Liu. Nucleophilic fluoroalkylation as an efficient avenue to achieve fluorinated polyimide monomers containing Csp3-R f from carbonyl compounds [J]. Journal of Polymer Science. 2020, 16(58), 2197-2210.
21. Chen YungChung, Su YuYang, Hsiao FengZh. The synthesis and characterization of fluorinated polyimides derived from 2′-methyl-1,4- bis -(4-amino-2-trifluoromethylphenoxy)benzene and various aromatic dianhydrides[J]. Journal of Macromolecular Science. 2020, 8(57), 579-588.
22. Zhang F. Synthesis and properties of low dielectric polyimide [D]. University of Chinese Academy of Sciences (Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences), 2020.
23. Fan Zhenguo, Chen Wenxin, Wei Shiyang, Liu Teng, Liu Siwei, Chi Zhenguo, Zhang Yi, Xu Jiarui. Quantitative structure-activity relationship of dielectric constant of polyimide and molecular structure design of low dielectric films [J].ACTA POLYMERICA SINICA . 2019, 2(50), 179-188.
24. Zhang P P. Preparation and properties of polyimide films with low dielectric constant [D]. Harbin Institute of Technology, 2018.
25. Song Ningning, GUAN Shaowei, Yao Hongyan, SHI Kaixiang. Synthesis and properties of polyimides containing crosslinked styrene side groups with low dielectric constant [A]. Polymer Science Committee of Chinese Chemical Society. Proceedings of the International Symposium on Polymer Science and Technology, Beijing, China [C]. Polymer Science Committee of Chinese Chemical Society: Chinese Chemical Society. 2017, 1.
26. Saritha B, Thiruvasagam P. Synthesis of diol monomers and organosoluble fluorinated polyimides with low dielectric[J]. High Performance Polymers. 2015, 7(27), 842-851.
27. R Ramani, R Ramachandran, G Amarendra, S Alam. Direct correlation between free volume and dielectric constant in a fluorine-containing polyimide blend[J]. Journal of Physics: Conference Series. 2015, 1(618).
28. Fei Chen, Debaditya Bera, Susanta Banerjee, Seema Agarwal. Low dielectric constant polyimide nanomats by electrospinning[J]. Polymers for Advanced Technologies. 2012, 6(23), 951-957.
29. Ankit Mishra, Lihua Chen, ZongZe Li, et al. Computational framework for polymer synthesis to study dielectric properties using polarizable reactive molecular dynamics[J]. Chemical Physics. 2020, 11, 1-12 .
30. van Duin A C T. Dasgupta S, Lorant F. et al. ReaxFF: A Reactive Force Field forHydrocarbons[J]. J. Phys. Chem. A 2001, 105, 9396-9409
31. YAO L B. Study on laser graphitization of carbon fiber and its molecular dynamics simulation [D]. Beijing University of Chemical Technology, 2018.
32. Rinaldi, D.; Rivail, J. Theor Chim Acta. 1974, 32, 243.
33. Rinaldi, D.; Rivail, J. Theor Chim Acta. 1974, 32, 57.
34. Rivail, J.; Carter, A. Mol Phys. 1978, 36, 1085–1097.
35. BODO MARTIN, PETER GEDECK, TIMOTHY CLARK. Additive NDDO-Based Atomic Polarizability Model[J]. INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY. 1998. 12, 1-25 .

512
513
514
515