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# **Effect of Monomer Structure on Energy Storage Characteristics of Polyimide Film**

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## SOMMARIO

Con il progredire della tecnologia ed il continuo aggiornarsi dell'industria, è stato difficile, per i materiali tradizionalmente usati per l'immagazzinamento di energia come la ceramica o il polimero, soddisfare gli elevati requisiti di prestazioni termiche o meccaniche in alcuni contesti applicativi all'avanguardia, come le apparecchiature di potenza in ambito aerospaziale e i condensatori ad alta potenza per l'immagazzinamento dell'energia. Le poliimmidi aromatiche, che svolgono un ruolo rilevante in molti campi grazie alle loro eccellenti proprietà termiche e meccaniche, sono una classe di materiali polimerici contenenti anelli di imide, inoltre, grazie alla loro varietà di strutture, hanno il potenziale per essere sviluppate in futuro in un nuovo importante materiale per l'immagazzinamento dell'energia. La progettazione e la sintesi di materiali poliimmidi con diverse tipi di struttura, le cui prestazioni saranno per forza di cose diverse, può essere ottenuta modificando la struttura dei monomeri dianidridi o diammine. La ricerca sulle caratteristiche di accumulo di energia delle poliimmidi causate dalle sue diverse strutture ha un importante valore teorico per la progettazione e la sintesi di nuovi materiali in poliimmide per l'accumulo di energia.

In questo lavoro, quattro strati di poliimmide con diverse strutture principali a catena sono stati sintetizzati sulla base della struttura Kapton, questi sono: PMDA-ODA, BPDA-ODA (introducendo una struttura bifenilica), BPDA-TRDA (introducendo un legame di etere), BPDA-TMDA (cambiando la posizione di sostituzione dei gruppi di amminoacidi sull'anello di benzene nella parte della diammina). Allo stesso tempo, sulla base di BPDA-TRDA, il trifluorometile è stato introdotto nella parte di diammina, dianidride, diamina e dianidride rispettivamente per ottenere tre strutture contenenti trifluorometile come gruppi secondari, che sono BPDA-FBDA, 6FDA-TRDA e 6FDA-FBDA. Per caratterizzare la struttura di tali poliimmidi sopracitate è stato effettuato un test di spettroscopia a raggi infrarossi. Le proprietà termiche sono state studiate da DSC e TGA. Sono stati inoltre effettuati test di spettroscopia dielettrica a banda larga e test di resistenza alla rottura per studiare le proprietà dielettriche di resistenza delle sette diverse poliimmidi. Sulla base dei risultati ottenuti, si è proceduto ad effettuare dei cambiamenti nella struttura monomerica per ottenere le caratteristiche di immagazzinamento dell'energia degli strati di poliimmide.

I sette strati di poliimmide hanno tutti eccellenti proprietà termiche, con temperature di decomposizione iniziali superiori a 500 °C e temperature di transizione vetrosa superiori a 200 °C. Quando la struttura bifenilica (BPDA-ODA) viene introdotta nella catena principale del monomero dianidride, la resistenza alla decomposizione del film di poliimmide sintetizzato viene significativamente migliorata mentre la costante dielettrica viene leggermente aumentata, la densità di immagazzinamento dell'energia viene dunque aumentata del 33,4% rispetto al PMDA-ODA. Quando il legame estereo viene introdotto nel monomero della diammina (BPDA-TRDA) o quando la sostituzione dei gruppi amminici sull'anello

benzenico della diammina viene cambiato da para-posizione a meta-posizione (BPDA-TMDA), la costante dielettrica e la resistenza alla rottura delle due poliimmidi si riducono allo stesso tempo, fattore che non favorisce l'aumento della densità di immagazzinamento dell'energia. L'introduzione di gruppi trifluorometilici nella parte dianidruro o diammina riduce leggermente la costante dielettrica della poliimmide a causa dell'aumento del volume libero. Quando i gruppi trifluorometilici vengono aggiunti nella parte dianidruro, la resistenza alla rottura dello strato di poliimmide viene ridotta, e viene quindi anche ridotta la densità di immagazzinamento dell'energia. Invece l'introduzione dei gruppi trifluorometilici nella parte di diammina (BPDA-FBDA e 6FDA-FBDA) aumenta notevolmente la tensione di rottura e la densità di immagazzinamento dell'energia, rispettivamente del 9,5% e del 18,9% secondo i risultati.

La ricerca in questo lavoro mostra che una maggiore densità di immagazzinamento dell'energia può essere ottenuta modificando la struttura della catena principale della poliimmide per ridurre il volume libero a disposizione e per aumentare la densità delle catene molecolari. Anche l'introduzione di gruppi secondari nella parte diametrale per modificare le caratteristiche "di trappola" della poliimmide risulta un metodo efficace per aumentare la resistenza alla rottura e aumentare la sua densità di immagazzinamento dell'energia.

**PAROLE CHIAVE:** Poliimmide; Struttura monomerica; Densità di immagazzinamento dell'energia

## ABSTRACT

With the advancement of technology and industrial upgrading, it has been difficult for traditional energy storage materials such as ceramic or polymer to meet the higher requirements on thermal performance or mechanical performance in some cutting-edge application scenarios, such as aerospace power equipment and high-power energy storage capacitors. Aromatic polyimides, which play an important role in many fields because of their excellent thermal and mechanical properties, are a class of polymer materials containing imide rings. Also, they have the potential to be developed into a new important energy storage material in the future because of the diversity of their structures. The design and synthesis of polyimide materials with different structures, whose performance will be different of course, can be achieved by changing the structure of dianhydride or diamine monomers. The research on the effect on the energy storage characteristics of polyimides caused by the difference of the structures has important theoretical value for the design and synthesis of new energy storage polyimide materials.

In this paper, four polyimide films with different main chain structures were synthesized based on the Kapton structure, they are PMDA-ODA, BPDA-ODA (by introducing a biphenyl structure), BPDA-TRDA (by introducing an ether bond), BPDA-TMDA (by changing the substitution position of the amino groups on the benzene ring in the diamine part). At the same time, on the basis of BPDA-TRDA, trifluoromethyl was introduced into diamine, dianhydride, diamine and dianhydride part respectively to obtain three structures containing trifluoromethyl as side groups, which are BPDA-FBDA, 6FDA-TRDA and 6FDA-FBDA. Infrared spectroscopy test was conducted to characterize the structure of polyimides mentioned above. The thermal properties were studied by DSC and TGA. Broadband dielectric spectroscopy test and breakdown strength test are conducted to study the dielectric properties and breakdown characteristics of the seven different polyimides. Based on the results of the experiments above, the effect of changes of the monomer structure on the energy storage characteristics of the polyimide films.

The seven polyimide films all have excellent thermal properties, with initial decomposition temperatures above 500 °C and glass transition temperatures above 200 °C. When the biphenyl structure (BPDA-ODA) is introduced into the main chain of the dianhydride monomer, the breakdown strength of the synthesized polyimide film is significantly improved and the dielectric constant is slightly increased, thus the energy storage density is increased by 33.4% compared with PMDA-ODA. When the ether bond is introduced into the diamine monomer (BPDA-TRDA) or when the substitution of the amino groups on the benzene ring on the diamine is changed from para-position to meta-position (BPDA-TMDA), the dielectric

constant and the breakdown strength of the two polyimides are reduced at the same time, which is not conducive to the increase of the energy storage density. The introduction of trifluoromethyl groups into dianhydride or diamine part will slightly reduce the dielectric constant of polyimide because the increasement of free volume. When trifluoromethyl groups are added into the dianhydride part, the breakdown strength of the polyimide film is reduced thus the energy storage density is reduced. But the introduction of trifluoromethyl groups into diamine part (BPDA-FBDA and 6FDA-FBDA) the breakdown voltage is increased greatly, and the energy storage density is increased by 9.5% and 18.9% respectively as a result.

The research in this paper shows that a higher energy storage density can be obtained by changing the main chain structure of polyimide to reduce the free volume and increase the packing density of molecular chains. Introducing side groups into diamine part to change the trap characteristics of polyimide is also an effective method to increase the breakdown strength and increase its energy storage density.

**KEY WORDS:** Polyimide; Monomer structure; Energy storage density

**TYPE OF THESIS:** Application Fundamentals

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## 1 PREFACE

With the increasing energy demand brought by the improvement of people's living standard, industrial upgradation and the progress on science and technology, the non-renewable fossil energy which is universally used now will be in shortage in the near future, and it has become the developing direction of the future energy industry that renewable distributed energy as the new principal energy, such as wind power, solar power and geothermal power gradually substitute coal.<sup>[1]</sup>Distributed energy has many advantages for example, outstanding energy efficiency, small energy loss, little environmental pollution, and it is economic. It is likely to greatly change the traditional energy production and consumption pattern, and it is also of great significance to the control of air pollution and the resistance to global climate change.<sup>[2]</sup>However, due to the disadvantages of distributed energy, such as dispersion, intermittency and randomness, there are also some technical problems about the application of distributed energy, such as low quality of power supply and difficulty direct in interconnection to the power grid. Therefore, it is of great significance to study the energy storage system with low loss and environmental friendliness for the further utilization of distributed energy. Nowadays, common energy storage system includes traditional physical energy storage (greatly restricted by geography and space)<sup>[3]</sup>, battery<sup>[4]</sup>, fuel cell<sup>[5]</sup>, the electrochemical capacitance<sup>[6]</sup>, dielectric capacitor<sup>[7]</sup>, etc., among which the dielectric capacitor has the highest power density thus it has a huge potentiality for the pulse power, hybrid cars, medical instruments and equipment, the advanced sensor field as well as many other energy storage application scenario.<sup>[8, 9]</sup>However, there is a bottleneck in the energy storage density of dielectric materials with excellent thermal properties, which greatly limits the application of capacitors in the energy storage field.<sup>[10, 11]</sup>Therefore, it is of great significance to study the energy storage characteristics of new dielectric materials.

For energy storage capacitors, the energy storage density of energy storage materials plays a decisive role in their energy storage characteristics, and the thermal and mechanical properties of energy storage materials also greatly limit the application scenarios of energy storage capacitors. Dielectric materials with high energy storage density have been developed and applied for more than half a century. At present, traditional dielectric materials applied to capacitors mainly fall into two categories: inorganic ceramic materials and polymer materials.<sup>[12, 13]</sup>Ceramic capacitors have high permittivity, but their disadvantages such as low breakdown strength, high forming temperature, difficulty in machining, poor organic compatibility and high density make it difficult to meet the requirements of large-scale energy storage equipment.<sup>[14]</sup>Compared with ceramic materials, polymer materials have higher breakdown strength, high reliability, better dielectric tunability, low density and good processing performance. The films produced by polymer materials have a large area, which is conducive to the manufacture of small and miniaturized capacitors.<sup>[15]</sup>However, currently polymer materials are limited by their low dielectric constant (usually below 10), and their energy storage density is not enough to support large-scale commercial applications. Therefore,

a large number of researchers have devoted themselves to the research direction of improving the energy storage density of polymer matrix composites.<sup>[13]</sup> Polyvinylidene fluoride (PVDF) and its copolymers have high dielectric constant, and the energy storage density of polyvinylidene-hexafluoropropylene (PVDF-HFP) matrix composites has been increased to 31.2 J/cm<sup>3</sup>.<sup>[16]</sup> However, due to the low glass transition temperature ( $T_g$ ) of polyvinylidene fluoride and other polymers, it is difficult to be used in aerospace power systems, advanced electronic equipment and high-power energy storage equipments where the temperature is usually very high.<sup>[17]</sup> Biaxially-oriented polypropylene (BOPP) film capacitors which is now commonly used in cars needs the cooling system control the temperature at around 70°C, which wastes a lot of energy and makes the equipment expensive and difficult to manufacture.<sup>[11]</sup> In conclusion, even if the PVDF composite material has high energy storage density, but their poorer performance at high temperature makes their application scope limited. To find and synthesize a polymer which has high thermal stability and high energy storage density is of great significance for the breakthrough in the application of polymer in energy storage capacitor and it is worth to do research on the direction.<sup>[18]</sup> Table 1-1 lists the general physical properties of high-temperature polymer materials used for dielectric materials: polyvinylidene fluoride (PVDF-CTFE), polycarbonate (PC), polyphenylene sulfide (PPS), polyetherether ketone (PEEK), polyetherimide (PEI), polytetrafluoroethylene (PTFE), fluorene polyester (FPE).<sup>[19]</sup> It is evident from Table 1-1 that polyimide materials (PI) can be used at a higher temperature than other common polymer materials in the table.

Table1-1 General physical properties of common polymer materials<sup>[19]</sup>

performance	PVDF - CTFE	The PC	PPS	PEEK	PEI	PTFE	FPE	PI,
Maximum operating temperature /°C	125	130	150	150	200	260	275	300
Relative dielectric constant	11	3	3.1	3.2	3.2	2.1	3.3	3.3
Tangent of medium Loss ( $\times 10^{-3}$ )	50	1.3	0.5	4	2	0.5	2.6	2
Tensile strength /MPa	51.7	65.5	248.2	27.6	96.5	20.7	65.5	34.5

Energy storage density refers to the electrical energy that can be stored and utilized in a unit volume of dielectric material, of which the unit is J/cm<sup>3</sup>. Generally speaking, energy storage density is used to characterize the energy storage performance of materials. The higher its value, the greater the energy density that the energy storage material can store and release.<sup>[20]</sup> The energy storage density is positively correlated with the field strength of the applied electric field. The closer the applied electric field is to the breakdown strength of the dielectric material, the higher the energy storage density is. When the electric field intensity of the applied field intensity is  $E$ ,  $dD$  represents the metavariable of the electric displacement vector  $D$ , and the slight change of energy density is  $E dD$ . The expression of energy storage density is shown in Equation (1-1).

$$J = \int_0^{D_{\max}} EdD \quad (1-1) \quad 1$$

Where:

$J$ —— the energy storage density  $/J \cdot \text{cm}^{-3}$ ;

$D_{\max}$ —— Electric displacement vector under saturation field intensity  $/C \cdot \text{m}^{-2}$ ;

There is a linear relationship between the electric displacement vector  $D$  and the applied electric field strength  $E$ . Equation (1-2) is the expression:

$$D = \varepsilon_r \varepsilon_0 E \quad (1-2) \quad 1$$

Where:

$\varepsilon_r$  —— relative dielectric constant;

$\varepsilon_0$  —— the dielectric constant of vacuum ,of which value is  $8.85 \times 10^{-12} \text{ F/m}$ ;

Thus, Equation (1-1) can be derived as following:

$$J = \int_0^{D_{\max}} \varepsilon_r \varepsilon_0 EdE \quad (1-3) \quad 1$$

As most polymers are linear dielectric materials, their relative dielectric constant is independent of the external electric field, which means that  $\varepsilon_r$  can be moved out of the integral part of the equation. Therefore, for linear dielectric materials, the energy storage density can be derived as Equation (1-4) :

$$J = \frac{1}{2} \varepsilon E^2 \quad (1-4) \quad 1$$

According to Equation (1-4), the energy storage density of a linear dielectric material is determined by the dielectric constant  $\varepsilon$  and the breakdown strength  $E_b$ .  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  are two typical linear dielectric materials, as are most polymers.

Therefore, the study of the breakdown strength and dielectric constant is an important direction for us to study the energy storage characteristics of polymer materials. If the breakdown strength or dielectric constant of the energy storage material can be greatly improved, high energy storage density can be obtained correspondingly.

As early as 1908, Bogert and Renshaw successfully synthesized aromatic polyimide for the first time in the laboratory using 4-aminobenzoic anhydride through a molten self-condensation reaction.<sup>[21]</sup>In 1955, Edwards and Robison, working for Du Pont, applied for the world's first patent on polyimide materials together, and polyimide has been used as commercial products ever since.<sup>[22]</sup>Up to 2000, there are more than 20 types of commercial polyimides and the research, development and production of those polyimides are mostly concentrated in the United States, Western Europe and Japan. There are some famous manufacturers in the world including Du Pont, GE, Amoco, BASF, Ciba-Geigy, Ube, Mitsui East Asia, Sumitomo Chemical, And Toray Industries, etc.<sup>[23]</sup>Due to the excellent comprehensive properties of polyimides as heat-resistant polymers, polyimides have been

slowly researched, developed and applied over the past century. Worldwide demand for polyimides is expected to increase at an average rate of about 10% in the next few years.<sup>[24]</sup>

Polyimide materials have attracted the attention of many scholars and achieved rapid development in the commercial field mainly because of their excellent comprehensive properties, which mainly include the following aspects:<sup>[24-26]</sup>

Compared with other polymer materials, the most outstanding performance of polyimide is its heat resistance, which is also the key to the rapid development and wide application of polyimide materials. As to the type of aromatic polyimides, because of their large molecular chain rigidity and strong inter-molecular forces, they tend to have high  $T_g$  which is usually higher than 200 °C and high initial decomposition temperature which is usually higher than 500 °C ( $T_s$ ). The polyimide synthesized by condensation reaction of 3,3',4,4'-biphenyl tetracarboxylic dianhydride and para-phenylenediamine has a high  $T_s$  of 600 °C, which is known to be one of the polymer materials with best thermal stability. The heat resistance can be further improved by the composite of polyimide and carbon fiber. At the same time, the thermal expansion coefficient of polyimide is extremely low, which is generally in the range of  $2 \times 10^{-5}/^{\circ}\text{C} \sim 3 \times 10^{-5}/^{\circ}\text{C}$ , thus it has also outstanding dimensional stability.

The mechanical properties of polyimide materials are very good, and generally the unreinforced resin matrix has a tensile strength higher than 100 MPa. The tensile strength and tensile modulus of Kapton polyimide films were 172.4 MPa and 2.96 GPa. The Upilex polyimide film has a tensile strength of 400 MPa and its tensile modulus is in the range of 3 GPa~4 GPa. It is worth mentioning that a fairly good mechanical performance for a long time in the temperature range of 200 °C~260 °C.

Traditional relative dielectric constant of polyimide materials generally between 3.0 ~ 3.6 and dielectric loss factor is around  $1 \times 10^{-3}$ . Also, the dielectric strength is 100 ~ 300 kV/mm and the mass resistance is about  $1 \times 10^{17} \Omega \cdot \text{cm}$ . Moreover, polyimide has excellent dielectric stability and can maintain stability over a wide range of frequencies and temperatures.

In general, polyimides cannot be dissolved in common organic solvents, but some polyimides can be dissolved in certain polar organic solvents. Polyimide has excellent hydrolysis resistance in dilute acid solution, oxidant and reducing agent resistance, chemical stability at high temperature is better than other polymer materials, but polyimide is not resistant to concentrated sulfuric acid, concentrated nitric acid and halogens. Polyimide has excellent anti-irradiation performance. When the absorbed dose reaches  $5 \times 10^7$  Gy, the mechanical strength of polyimide film remains above 86%. After electron irradiation at  $1 \times 10^8$  Gy, its mechanical strength retention rate can be 90%.

Polyimides are also non-toxic, biocompatible, flame retardant (polyimides are self-extinguishing materials, the residual carbon rate is usually higher than 50% after burning at high temperature, and the smoke rate is low) and ultra-low temperature resistance (they can maintain a certain mechanical strength in liquid nitrogen).

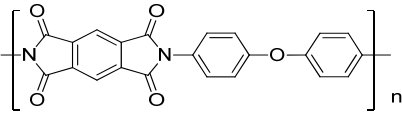
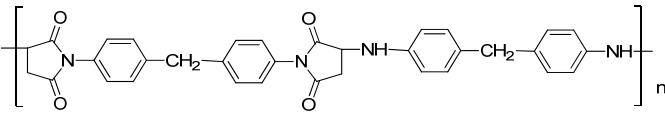
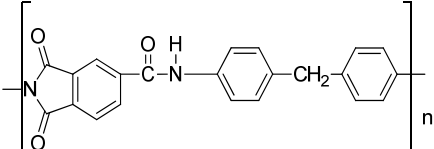
Because polyimide has the above excellent comprehensive properties, it has a wide range of applications that other polymers cannot match. Currently, polyimides are used as thin films,

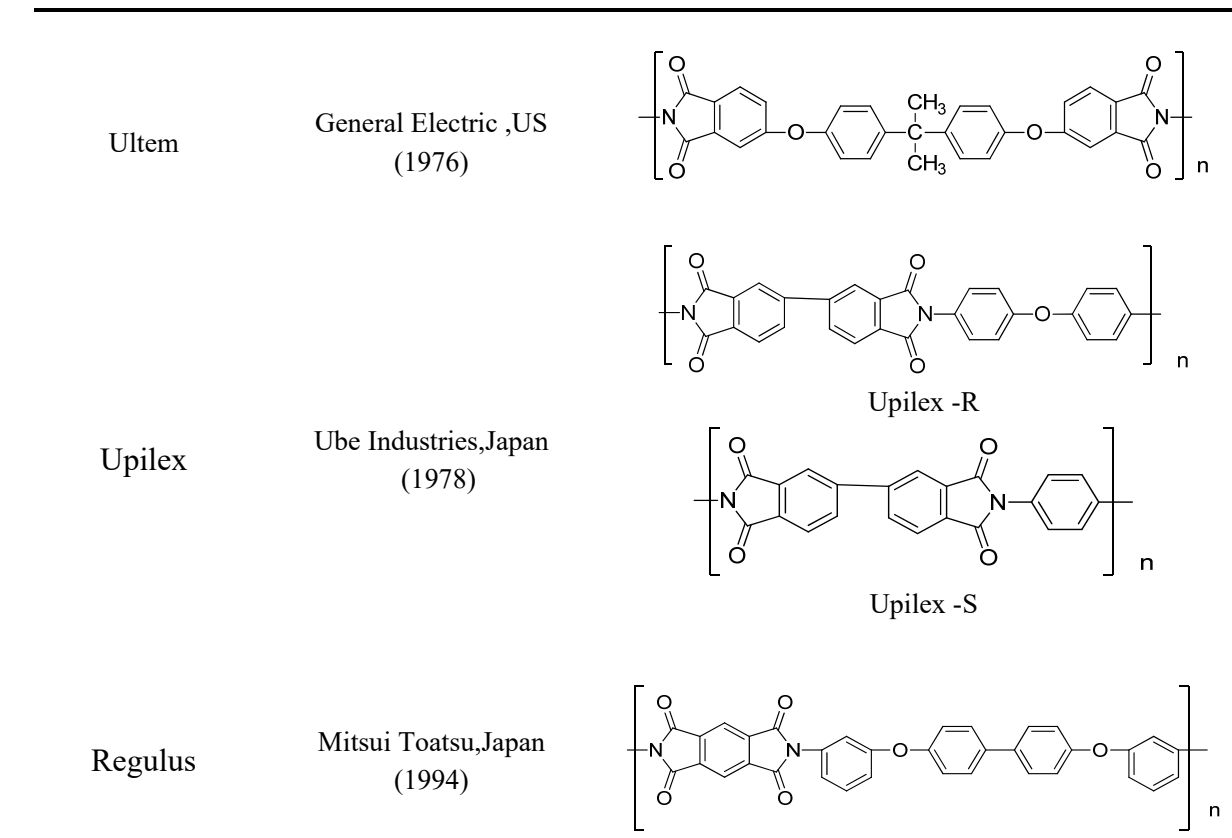
coatings<sup>[27]</sup>, advanced composites<sup>[28, 29]</sup>, fibers<sup>[30, 31]</sup>, engineering plastics, foam plastics<sup>[32]</sup>, adhesives<sup>[33]</sup>, separation films<sup>[34, 35]</sup>, photoresist<sup>[36, 37]</sup>, optical waveguide materials<sup>[38, 39]</sup>, inter-layer insulation and packaging materials for integrated circuits<sup>[40]</sup>, biocompatible materials<sup>[41, 42]</sup>, proton transfer films in fuel cell and so on. <sup>[23, 26]</sup>Polyimide has very outstanding performance in the application fields mentioned above. In recent years, due to the constant promotion of modification work on traditional polyimide materials and the increasing demand for new materials along with the emerging of new industries, polyimide materials glow its vitality with great potential for application in the emerging industry in the future.

The common commercial polyimides and their structural formulas are shown in Table 1-2.<sup>[24]</sup> Commercial polyimides produced by different companies have different properties and are suitable for different scenarios. In addition to the influence of different production processes, this difference in performance is also related to the different molecular structure of polyimide produced by each company. As can be seen from Table 1-2, the molecular structures of various commercial polyimides vary greatly.

At present, polyimide materials are widely known for their various structures, poor properties and USES. In general, polyimides are synthesized by monomers which are widely sourced and easy to be synthesized. Polyimides of different structure can be synthesized by different polymerization ways and methods or different processes. At present, the synthesis methods of polyimides can be roughly divided into two categories according to whether the monomers contain imide rings: the first category is the imide rings formed in the polymerization process, and the second category is the direct condensation of the monomers with imide rings, rather than the imide in the polymerization process.<sup>[26]</sup> The following is a brief introduction to several synthesis methods:

Table 1-2 Common commercial aromatic polyimides-<sup>[24]</sup>

Name of commercial aromatic polyimides	Research and development institutions	Chemical structure
Kapton	Du Pont ,US (1961)	
Kerimid 601	Rhone-poulenc, France (1969)	
Torlon	Amoco Corporation ,US (1976)	



The diamine monomer and the dianhydride monomer are dissolved organic solvent with a high boiling point in proportion at the same time, the commonly used solvent is usually phenols, such as m-cresol, p-chlorophenol, etc. At the temperature of 150 °C ~200 °C or melting state, the two monomers polymerize directly and the method to prepare polyimide is called one-step method.<sup>[43]</sup> This is because the precursor polyamide acid (PAA) is not synthesized in the preparation process and the polyimide is generated by direct condensation of two monomers. Since condensation polymerization is a reversible reaction that produces water, removing water from the reaction system timely is a very effective way to improve the conversion rate in the one-step reaction process. Although the one-step process is simple, it has significant limitations -- it requires high temperature and is only suitable for a small number of polyimides soluble in certain organic solvents. The reaction principle of the one-step method is shown in Fig. 1 Fig. 1-1 The diagram of the synthesis of polyimide using one-step method 1.

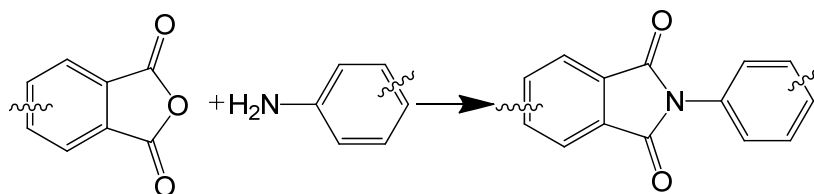


Fig. 1-1 The diagram of the synthesis of polyimide using one-step method

First of all, dissolve the same amount of diamine monomer and the dianhydride monomer evenly in aprotic polar solvent, such as N-Methyl pyrrolidone (NMP), N, N - dimethyl formamide (DMF) and N, N - dimethyl acetamide (10-channel DMAc) and so on. Then pre-polymerize at room temperature or low temperature (because the reaction is exothermic

reaction, can use ice-water bath to improve the conversion rate of reaction). After the preparation of precursor polyamide acid, polyamide acid is dehydrated and cyclized into polyimide through the thermal midization or chemical midization.<sup>[26, 44]</sup>The two-step method has the advantage that the temperature conditions are easy to meet and is the most commonly used preparation method for polyimide. However, the two-step method also has its disadvantages as the sample obtained by the two-step method is restricted by the reactivity of raw materials, so it is difficult to obtain polyimide with higher molecular weight. Meanwhile, the precursor polyamide acid produced in the first step has low stability, high possibility of oxidation and hydrolysis, as a result PAA solution is difficult to preserve.

The reaction principle and steps of the two-step method are shown in Fig. 1-2.1

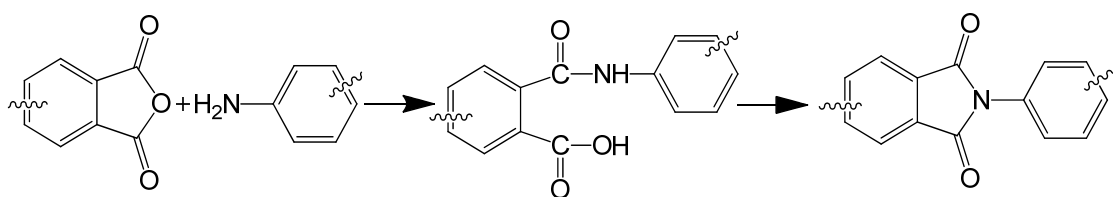


Fig. 1 2 The diagram of the synthesis of polyimide using two-step method1

The reaction principle and steps of the three-step method are shown in Fig. 1-3.1

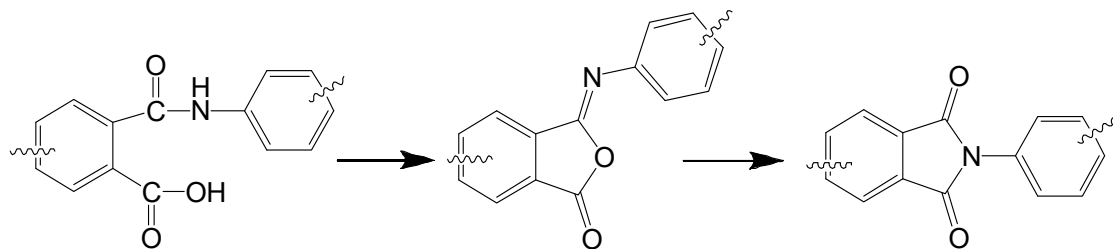


Fig. 1 3 The diagram of transformation from polyisoimide to polyimide

In the first step of the two-step method, the diamine and the dianhydride monomer are dissolved in a polar solvent and the solution of polyamide acid is obtained by polymerization.<sup>[45]</sup>Different from the two-step method, there is no direct imidation of polyamide acid but polyisoimide is produced with the addition of dehydrating agent. Common dehydrating agents include dicycyl carbimide, etc. Then the polyisoimide solution is placed at the temperature of 100~250°C and isomerize to obtain polyimide. The precursor polyisoimide is also widely concerned because of its excellent solubility and low glass transition temperature, which indicates it is easy to process and shape.

Vapor deposition method is usually used for the production and preparation of polyimide films. Under the condition of high vacuum, both the dihydride and diamine monomers are easy to sublime. By vapor deposition method, a polyimide film can be formed on the material surface conveniently and it is called VD PI. The preparation process is to transfer the vapor of the equal amount of the diamine monomer and the diamine monomer separately into the mixing chamber at high temperature, and then mix them together to form a thin film. Compared with the above methods, the polyimide coating is directly generated by monomer at high temperature without the involvement of solvent.<sup>[46]</sup>The film prepared by vapor deposition has

better thermal stability, but it is needed to provide high temperature environment so the preparation cost is high and the control of the reaction is difficult.

All the methods above belong to the first category. In the second category, polyimides are formed from monomers containing imide rings through a series of reactions. These reactions include the use of dihalophthalimide or dinitrate. The nucleophilic substitution polymerization between the phthalimide and the alkali metal compounds of bisphenol or bithiophenol synthesizes polyimide,<sup>[47]</sup> and the polyimide is synthesized by imide exchange reaction.<sup>[48]</sup> Condensation polymerization of dihalides and diboric acid compounds containing imide rings into polyimides, synthesis of polyimides, etc. through the nucleophilic substitution reaction of alkali metal compounds of tetraimide and dihalides.<sup>[49]</sup>

In addition to van der Waals force, Charge Transfer Complex (CTC) is also formed in the synthesis of polyimide by using dianhydride and diamine monomer. In the polyimide molecular chain, the diamine chain can be used as an electron donor (diamine chain), and the dianhydride chain can be used as an electron acceptor, and the two are arranged alternately. At this time, the two will have the effect of charge transfer within the molecular chain or between the molecular chains due to the difference of electron affinity, thus forming a charge transfer complex. Mixed Layer Packing (MLP) is formed when adjacent polyimide molecular chains are mainly packed with charge transfer. Its structure is shown in Fig. 1-4, and the arrow represents the direction of electron transfer.

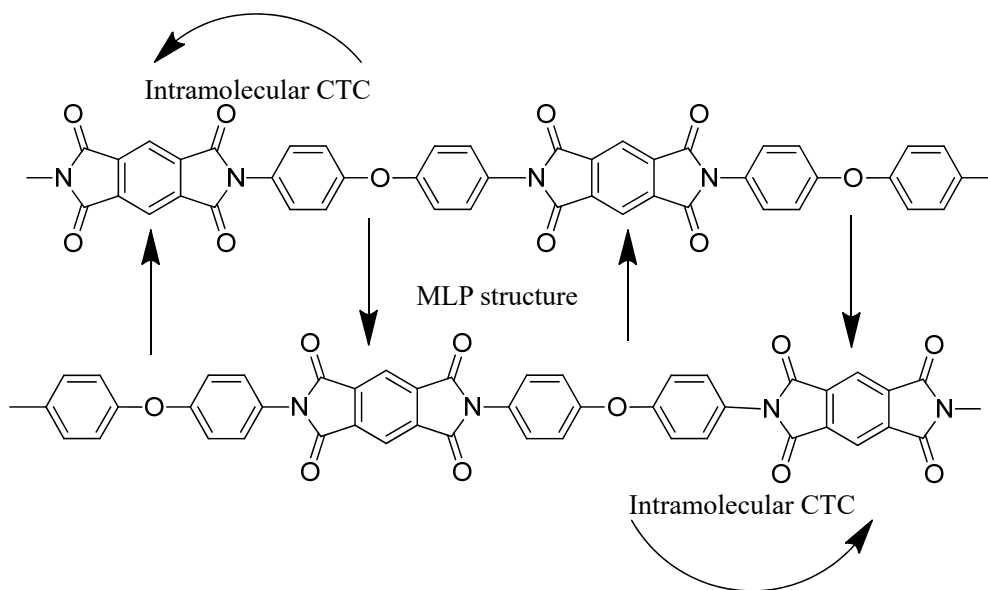


Fig.1-4 Intramolecular charge transfer complexes and interlayer stacking structures of polyimide

When the monomer structure of diamine or dianhydride changes, if the conjugated system increases, in addition to making the polyimide polymer chain more rigid, it will increase the formation of charge transfer complex, so that the degree of stacking between the mixed layers of polyimide is closer. The strength of CTC depends on the monomer structure. When the dianhydride chain has a strong electron absorbing ability or diamine has a strong electron giving ability, the internal charge transfer complexation of polyimide is stronger.<sup>[50]</sup> Therefore, the formation of intermolecular and intramolecular charge transfer complexes and the physical



properties of polyimides will be affected by the synthesis of polyimides with different diamines and dihydride monomers. When the properties of polyimide materials synthesized from monomers with different structures are studied, the differences of the properties caused by the different structures of polyimide molecules are another aspect to be considered.

By far, there have been more than 20 kinds of polyimide in the world, and it has gradually developed into one of the most widely used materials in heat resistant polymer materials. Therefore, once the energy storage density of polyimide materials can be greatly improved, the application of polyimide in the field of energy storage has a broader application prospect than other polymer materials. In the subject of how to improve the permittivity of polyimide, many scholars have made a lot of attempts, including filling, compounding, changing the process and so on. However, further research is needed to reveal the influence of changing the structure of monomers on the permittivity, breakdown strength and dielectric loss of polyimide. At present, there are few studies on the energy storage characteristics of polyimides, and most of them are based on the structure of several commercial polyimides around the dielectric constant or the breakdown strength.

Treufeld I et al. systematically studied a series of polyimide samples with high polar nitrile groups and found that adding a nitrile dipole to the polyimide structure would increase the dielectric constant.<sup>[51]</sup> In particular, introducing three nitrile groups on the basis of the diamine unit is more effective in increasing the dielectric constant than introducing a nitrile group. The dipole moment of the dihydride also plays an important role in polar polyimide samples with three nitrile groups. As the dipole moment of the dihydride part increases in the order of PMDA, ODPA, 6FDA and BTDA, the enhancement of the dielectric constant gradually decreases, indicating that the dihydride and diamine should be arranged in opposite directions and the dipole moments cancel each other at the molecular scale. However, although the dielectric constant of these polyimide samples containing nitrile groups was increased, the dielectric loss was also increased, which can be attributed to the direct attachment of nitrile groups to the polyimide backbone.

Chen GR et al. designed a KTN/PI composite film with a three-layer structure.<sup>[52]</sup> Polyimide as substrate can give the composite film excellent thermal stability. PI intermediate layer with high breakdown strength and low dielectric constant was introduced into the breakdown path to improve the electric field distribution of the composite film, while the outer composite layer filled with KTN nanoparticles with high dielectric constant could improve the energy storage density. The three-layer KTN/PI composite film has high discharge energy density and charge and discharge efficiency, and has low conductivity loss under high electric field.

Ding A preparation of A series of polyimide polymer nanocomposites, the doping of inorganic nano filler with different dielectric constants and band gap  $\Delta E$ .<sup>[53]</sup> The breakdown strength of typical dielectric composite decreases with the addition of high dielectric constant dopants, but the breakdown strength of the series polyimide composite is greatly increased compared with that of pure polyimide. Designed to work in the weak current field and the room temperature of the dielectric constant of dielectric fillers in composite materials in determining

capacitance characteristics plays an important role, but high temperature precisely, by contrast, packing band gap  $\Delta E$  dominates its capacitance at high temperature properties. High field polymer composites. Adding inorganic filler having a large band gap  $\Delta E$  will significantly reduce the conduction current, resulting in high electric field and high temperature with high breakdown voltage of the dielectric composite materials. Incorporation of  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$  at the same time, the big  $\Delta E$  and appropriate under the synergy of the dielectric constant of the polyimide matrix composites, the optimal capacity under the high temperature performance. This work reveals the significant effect of inorganic nano-fillers on the high temperature capacitance properties of polymer composites and elucidate the rational design of scalable dielectric polymer composites for power storage in extreme environments.

Li Hongyan et al. synthesized polyimide/nanocomposite films by in situ dispersion polymerization.<sup>[54]</sup> The in situ dispersion polymerization method can make the nanoparticles evenly dispersed in the polyimide matrix. Nano-tio particle and polyimide can be compounded at the nanoscale. It is found that changing the doping concentration of  $\text{TiO}_2$  nanoparticles during preparation will affect the dielectric properties of polyimide/nanocomposite films. With the increase of nano- $\text{TiO}_2$  doping, the relative dielectric constant of polyimide/nanocomposite films will increase, and the volume resistivity, electrical strength and tangent of dielectric loss Angle will deteriorate to different degrees. However, increasing the doping amount of nano- $\text{TiO}_2$  particle will significantly improve the corona resistance of polyimide/nanocomposite film materials.

Because for the richness of the monomers using to synthesize polyimide and diversity of synthetic route and process, by the synthesizing or selecting different monomers of different structures can be used for the synthesis of different structure of polyimide materials. As a result the performance of the polyimides with different structure will inevitably lead to the diversity of performance, which makes it feasible to design suitable polyimide materials for different application scenarios. The study of the influence of changing monomer structure on polyimide energy storage characteristics has great significance for the molecular structure design of polyimide, and has certain significance and value as reference for designing of the molecular structure of polyimides and even other polymer materials. More importantly, revealing the difference in energy storage characteristics of polyimides of different structures and making a deep discussion on the causes of their production can provide a certain reference for the research of a new generation of dielectric energy storage materials with high thermal stability, high energy storage density, high charging and discharging efficiency, low loss and high reliability. As to the modification of pure polyimide, the research now mostly focused on the molecular structure of change for dissolving properties, optical properties, thermal properties and the influence of mechanical properties, and few research is about the influence of the molecular structure change on the energy storage characteristics, and often from one side, which is the influences on breakdown voltage or the influences on dielectric constant. Thus the influence of changing monomer structure on dielectric properties of polyimide materials combined with breakdown characteristic research is of great significance for the study of energy storage properties of polyimide. In this paper, the focus of the discussion will be the

difference and the reasons of the breakdown strength and dielectric constant between polyimides synthesized from monomers with different structures, and the study will be conducted to improve the energy storage density of polyimide films from the perspective of changing the molecular structure of polyimide.

Polyimide, as a kind of functional polymer material, besides has the outstanding thermal performance and the most excellent comprehensive performance, in many industrial areas, such as in aerospace, fine chemical industry and microelectronic industry and so on, has the extremely widespread application, the application in some special situations other materials has an irreplaceable role. However, limited by energy storage density and production cost, polyimide has great potential in the field of energy storage. Because of the diversity of synthesis methods and structures, it is feasible to select, design and synthesize polyimide materials with satisfying performance requirements according to different application scenarios and application conditions. Monomer largely determines the nature of various properties of polyimide materials, through the synthesis design and choose different dianhydride and diamine monomer in material structure change will lead to the change of material performance, to systematically study the change and the reasons for polyimide application has very important significance in the field of energy storage.

In order to maintain the high thermal stability of polyimide materials, the dianhydride and diamine monomers selected in this paper are aromatic monomers. In order to improve the energy storage density of polyimide, a method of molecular structure modification was proposed to synthesize polyimide materials by two-step solution polycondensation with different aromatic dianhydride and diamine. Basic idea is to conjugate biphenyl structure or flexible join key ether bond is introduced into the molecular main chain, change in the main chain amino on the benzene ring to replace the position and will introduce three fluorinated methyl side group, have different structure of polyimide materials, while maintaining the performance of polyimide material heat-resisting, looking for high energy storage density, low dielectric loss of polyimide materials of excellent comprehensive performance. More importantly, in the hope that more systematic research in this paper, the preparation of polyimide materials structure and the relationship between the energy storage characteristics, explore the potential application of polyimide materials in areas such as energy storage capacitor, the development and application of polyimide materials provide valuable research results and new design ideas, to provide certain reference other polymer molecular design.

The research contents and key problems to be solved in this paper are as following:

(1) From the perspective of molecular structure design, the idea of introducing biphenyl structure, changing the substitution position of amino group on the benzene ring, introducing ether bond and introducing trifluoromethyl lateral group was adopted to synthesize seven different polyimide films by two-step method by selecting three aromatic dianhydride and four aromatic diamine monomers with different structures.

(2) The seven polyimide films with different structure prepared in this work are tested respectively by infrared spectrum analysis, differential scanning calorimetry, thermogravimetric analysis, DC breakdown performance analysis, broadband dielectric

spectroscopy analysis and thermal stimulation current analysis, then the difference of the thermal performance and energy storage properties of polyimide film sample is compared and the law of the influence on energy storage characteristics of polyimide films brought by the change of the structure is analyzed.

## 2 PREPARATION AND PROPERTY TEST OF POLYIMIDE FILMS

Thin film samples are less susceptible to strain than the bulk samples and they are easy to prepare. Also a large applied electric field can be obtained at a relatively low voltage, which is conducive to the study of its energy storage characteristics when the sample is thin. Therefore, aromatic polyimide film samples which have outstanding heat stability are selected as the object of research in this work. Take the advantages of that it's easy to choose different monomer to synthesize different film samples with different structure, this work aims to improve its dielectric constant or breakdown voltage of the PI films by changing the structure of the monomers and ultimately achieve in improving the energy storage density under the premise of maintaining its thermal stability. This chapter mainly introduces the process of preparing polyimide film samples by two-step method and the related content of performance test, including the relevant information of Fourier transform infrared spectroscopy, thermal performance test, broadband dielectric spectroscopy test, breakdown voltage test and thermal stimulation current test.

Based on the advantages of the two-step method and the feasibility of preparation in the laboratory, the two-step method mentioned in chapter 1 is adopted to prepare polyimide films and builds a platform for the preparation of polyimide film samples in this paper. Because the purity of raw materials and solvents is an important condition to improve the film-forming property in the sample preparation, and it has an important influence on the properties of the prepared films, the dihydride and diamine monomers selected in the experiment in this paper were both products with high purity. Table 2-1 shows the names and models of instruments used in the polyimide film sample preparation platform. The drug and solvent information of diamine and dianhydride monomers selected in sample preparation are shown in Table 2-2 and Table 2-3.

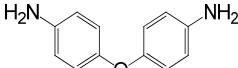
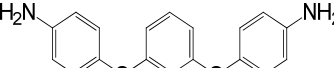
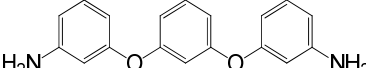
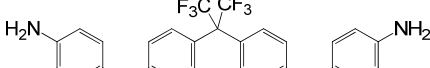
Table 2-1 Information about the equipment for the preparation of the PI films

The name of the instruments	Models
Thickness gauge	YHT (flat head 0.001mm)
Magnetic stirrer	IKA Topolino
Analytical balance	METTLER TOLEDO ME204E
Programmable oven	Type 101
Pipetting device	JOANLAB5000 $\mu$ L
High power NC ultrasonic cleaner	KQ - 200 type kde
Stirring heater	Type 78-1

This section will introduce the equipment used in each step and the standard operation process of each step respectively from the three steps of preparation of polyacryl acid solution, film formation, and defilming and drying.

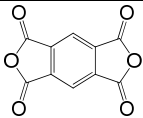
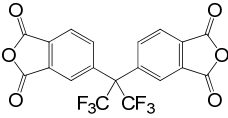
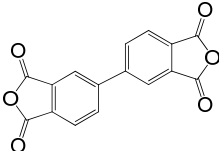
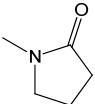
The platform for the preparation of polyamide acid is shown in Fig. 2-1. The three-necked, round-bottomed flasks are connected in turn with latex tubes and the mouth in the middle of each three-necked, round-bottomed flasks are sealed with dry tubes filled with calcium chloride particles (the two ends of the calcium chloride particles are blocked with a small amount of cotton to prevent contamination of the flyers with calcium chloride powder). Each flask with a flask clamp is fixed on the frame, a magnetic stirrer is placed at the bottom of the flask, keep the rotation of diamond magneton in the process of preparation so that the monomer fully dissolved in solution and homogeneous reaction, which can improve the reaction rate and make the effective contact of monomer molecules and improve the molecular weight of the polyamide acid generated in the reaction. A flow meter is connected on the left and right sides of the device. The flow meter on the right side is directly connected with the nitrogen bottle to adjust the nitrogen flow rate. There are two functions of the left flowmeter. One is to detect the air tightness of the device, the other is to ensure that there is always nitrogen flow through the device during the sample preparation.

Table 2-2 Diamine monomers used in this study2-

Name	Structure of short form	Abbreviation	Specifications	Source
4,4'-oxydianiline		ODA	AR	Alfa Aesar
4,4'-(1,3-Phenylenedioxy)dianiline		TRDA	AR	TCI
3,3'-(1,3-phenylenebis(oxy))dianiline		TMDA	AR	TCI
2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane		FBDA	AR	Alfa Aesar

Nitrogen gas has been introduced during the experimental preparation process. First, the polyamic acid solution will also be hydrolyzed. The reason is that the amide group in the polyamic acid will spontaneously catalytically cleave, and the resulting anhydride will be due to the presence of moisture in the solvent (dianhydride and the water generated during the reaction of the diamine monomer in the flask) is hydrolyzed, so that the anhydride can no longer react with the amine to regenerate the amide ; on the other hand , the nitrogen flow takes away water and will result in the polycondensation reaction proceeding in the positive direction and increasing the molecular weight of the polyamic acid produced by the reaction to achieve the ultimate goal of increasing the molecular weight of the polyimide sample. When the molecular weight of the synthesized polyamic acid is not large enough, the film forming property is greatly affected, in the second step of thermal imidization of the case where the film will be prone to fragmentate, so this step and standards for increasing the molecular weight of polyamic acid is crucial.

Table 2-3 Dianhydride monomer and solvent used in this paper2-

The name of the reagent	Structure of short form	Abbreviation	Specifications	Source
1,2,4,5- Benzenetetracarboxylic anhydride		PMDA	AR	Alfa Aesar
4,4'- (Hexafluoroisopropylidene) diphthalic anhydride		6FDA	AR	Alfa Aesar
3,3',4,4'- Biphenyltetracarboxylic dianhydride		BPDA	AR	TCI
N-methylpyrrolidone		NMP	GC	Macklin

The specific experimental steps and operation of preparation of polyamide solution are as follows:

(1) Take the cleaned and dried flasks, latex tubes and drying tubes from the oven at 60°C and connect them as shown in Fig. 2-1;

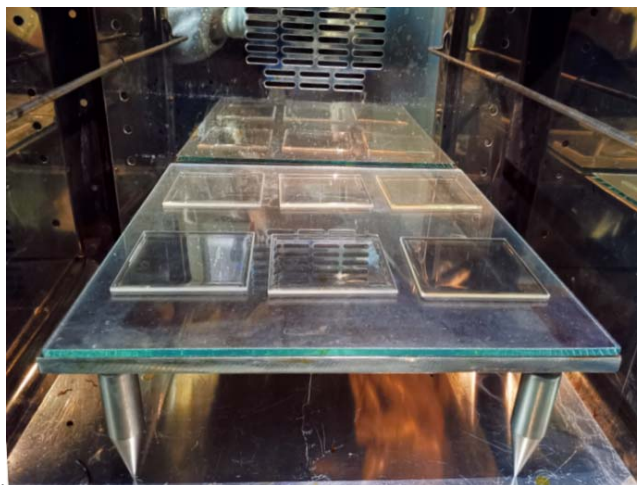


Fig. 2 1 Diagram of production equipment for polyamic acid

(2) Put the dry NMP solvent into a three-mouth flask with a pipette, put the diamond-shaped magneton, and turn on the magnetic stirrer. 1 mmol diamine was weighed with an analytical balance and then rolled up with weighing paper and moved into the three-mouth flask. When the diamine was completely dissolved after stirring, 1 mmol dianhydride was placed into a three-mouth flask. The concentration of the solution is 12%. Seal the mouth of the flask with a drying tube. At higher room temperature, an ice bath was used to obtain the polyamide acid with a higher molecular weight. After 24h of reaction, the solution was transferred to the syringe with filter tip by dropper, and the pure polyamide acid solution was obtained after filtration. 1

In this paper, polyamide acid solution was transferred into polyimide films by fluidization and thermal imidation. The platform of thermal imidation is shown in Fig.2-2. In the

temperature-controlled air blast drying oven, the glass plate with a smooth surface (horizontal, angle error  $\pm 0.04^\circ$ ) and large surface is placed on the iron table with three rotating legs at the bottom. The clean and dry square quartz glass plate (100 mm $\times$ 100 mm $\times$ 1 mm) is placed



successively on the large glass plate.

Fig. 22 Diagram of thermolimide unit2-2

The programmable air blast drying oven are as follows: rapidly heat to 80 $^\circ\text{C}$  from the room temperature, heat to 80 $^\circ\text{C}$  and maintain the temperature for 3 hours, heat to 120 $^\circ\text{C}$  and maintain the temperature for 30 minutes, heat to 150 $^\circ\text{C}$  and maintain the temperature for 30 minutes, heat to 180 $^\circ\text{C}$  and maintain the temperature for 30 minutes, heat to 250 $^\circ\text{C}$  and maintain the temperature for 30 minutes, heat to 300 $^\circ\text{C}$  and maintain the temperature for 30 minutes, and cool down to room temperature with the oven naturally. There are two purposes of the heating: one is to evaporate the solvent nitromethyl pyrrolidone in the polyamide acid solution and the other is to dehydrate and cyclize the polyamide acid to form polyimides. At 300 $^\circ\text{C}$ , the thermolimide process was basically completed. It is important to ensure the complete thermalimide of polyimide, as this greatly affects the mechanical, thermal and dielectric properties of the final polyimide film.

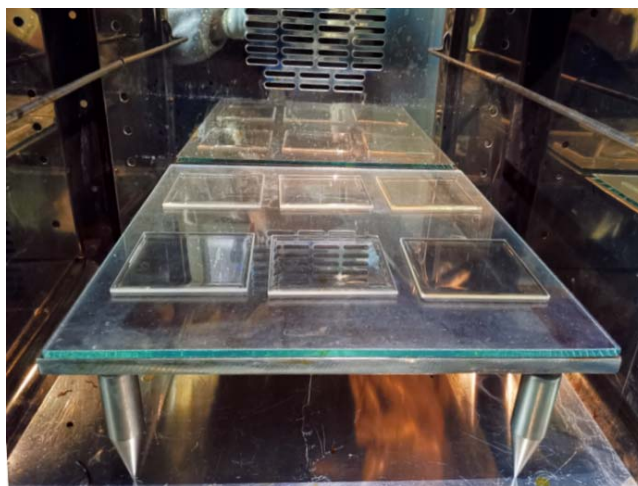


Fig. 22 Diagram of thermolimide unit2-2

The specific experimental steps of polyimide film preparation are as follows:



- (1) Clean the programmable air blast drying oven and set up the heating procedure
- (2) Use the digital display electronic gradienter with precision of  $0.02^\circ$  and adjust the support knob of the iron platform, so that the glass plate is placed horizontally (x direction and Y direction of the glass plate are kept to indicate the number of  $0.00^\circ$  ), and place the square quartz glass plate on the glass plate.
- (3) Drop the polyamide acid solution obtained in the previous step onto the square quartz glass with an eyedropper. Pay attention to avoid the formation of bubbles in the whole process. Close the programmable air blast drying oven and start the heating procedure.

Fig. 2-3 shows the stripping device after polyimide film formation. Place the quartz glass plate with polyimide film attached in the second step on a stirring heater and heat it to  $90^\circ\text{C}$  in water bath, then cool naturally with distilled water. After the film comes off, use alcohol to clean the film with non-woven fabric and keep the samples in clean oven at  $60^\circ\text{C}$  for more than 48 h. Place them into the transparent seal bag and classify them with label until performance test. Fig. 2-4 shows the polyimide film samples prepared in this week, with a thickness of about  $40\ \mu\text{m}$ .

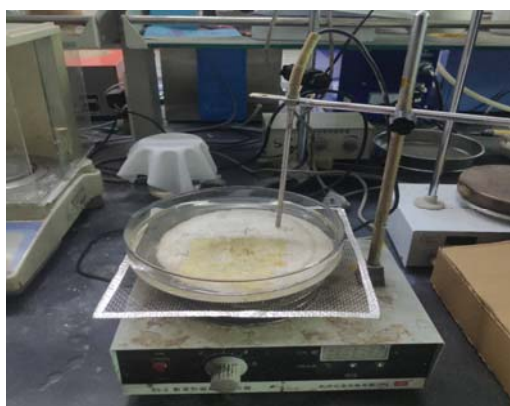


Fig. 23 Drawing of debraning device2-



Fig. 24 Polyimide film sample diagram2-

In order to compare the difference of the energy storage characteristics of polyimide synthesized by different monomers, it is necessary to conduct material characterization test and related performance test for the prepared polyimide film samples, including structural characterization, thermal performance test, wideband dielectric spectrum test, thermal stimulation current test and breakdown performance test. This section mainly introduces the test equipment and test methods for polyimide film samples.

In this section, Fourier transform infrared spectroscopy, thermal performance test, broadband dielectric spectroscopy test, breakdown voltage test and thermal stimulation current test are briefly introduced respectively. The experimental conditions and methods of each experiment are as follows:

Fourier Transform Infrared (FTIR) is an analysis method to obtain the molecular structure of substances and to distinguish compounds by analyzing the relative vibration of intramolecular chemical bonds and the rotation of functional groups, which is an effective means of determining the molecular structure and functional groups of substances.<sup>[55]</sup> Material of each

functional groups or chemical bond has its specific rotation frequency of the vibration frequency or, with continuous frequency of infrared radiation material, and the sample under test of some functional groups or chemical bonds of the rotation frequency of the vibration or the same infrared light will be absorbed, so as to form the absorption peak, through the test equipment will absorb infrared data records for the infrared absorption spectrum. To the experiment of the preparation of polyimide film sample testing, the characteristics of molecular structure of qualitative identification of the preparation of polyimide film sample, using Bruker production of Fourier transform infrared spectrometer (IRpresitge - 21) an analysis of the ir test sample, set the spectral range is 4000 ~ 400 cm, single attenuated total reflection method is used to scan 32 times.<sup>-1</sup>

Glass transition is the intrinsic qualities of crystalline polymer material, is the macro level high polymer materials under the internal microscopic movement of molecular chain form change, its processing technology on material and various performance has a direct influence, so has been glass transition temperature is an important part of the study of polymer materials. In order to test Tg of polyimide samples, differential Scanning Calorimetry (METTLER TOLEDO DSC type 822E) was used for supermarket Scanning Calorimetry (DSC) test. A small film sample (about 8 mg) was weighed by an analytical balance and placed into the aluminum crucible. In the atmosphere of nitrogen, the sample was raised from room temperature to 350°C at a heating rate of 10°C/min to measure the change of heat flow in this process.

When the ambient temperature rises, the large molecules in the material begin to crack. At this time, the temperature is the thermal decomposition temperature of the material, which is one of the important thermal properties of the polymer and the highest temperature in the molding process of the polymer material. Thermal Gravimetric Analysis (TGA) was used to measure the Thermal stability of polyimide film samples. The experimental instrument was TGA/SDTA851. A small film sample (about 8 mg) was weighed by an analytical balance and placed in a ceramic crucible, which increased from 50°C to 900°C. The remaining mass of the sample was measured in a nitrogen atmosphere.

In order to obtain the broadband dielectric spectroscopy of polyimide samples, the wideband dielectric spectrum testing system (Novocontrol Concept 80) was used for testing. The sample to be tested was cut into a round sample with a diameter of 30mm. After ultrasonic cleaning and drying treatment, the upper and lower surfaces of the round sample were sprayed with gold, and the sample was clamped with an electrode with a diameter of 30mm and put into a temperate-controlled chamber for the test of variable temperature wideband dielectric spectrum. The test temperature range was set as 20°C~200°C, and the interval was 20°C. The test frequency range is 10<sup>-2</sup> Hz~10<sup>6</sup> Hz.

In order to test the breakdown performance of polyimide film samples, the BAUR company BDJC-100 kV type automatic breakdown meter is used to conduct the dc breakdown voltage testing of polyimide film sample. The film samples are immersed in mineral transformer oil at room temperature and clipped by the ball-ball electrode. The rising rate of voltage is set to 1 kV/s. For each sample, 20 datas of breakdown voltage are recorded and the

distance between any two testing points is more than 10 mm to avoid the surface flashover. The two-parameter Weibull distribution was used to analyze the breakdown performance of the samples after the calculation of breakdown strength, and the electric field intensity when the probability of failure is 63.2% is used as the breakdown strength of the samples.

The breakdown strength of polymer is dispersed due to the abnormal internal structure of the sample, and it is usually treated with Weibull Distribution. Weibull distribution, which was proposed by Swedish engineer Weibull in the early 1950's. It has strong fitting ability for various types of life test data and can be used as the theoretical basis for reliability analysis and life test.<sup>[56-58]</sup> According to the different number of parameters, it can be divided into single parameter, two parameter and three parameter Weibull distribution. In breakdown life analysis, two-parameter Weibull distribution is usually selected, and its distribution function is expressed as Formula (2-1) :

$$F(x) = 1 - \exp \left\{ - \left( \frac{x}{\alpha} \right)^\beta \right\} \quad (2-1)$$

where:

- $\alpha$  — Scale parameter;
- $\beta$  — Shape parameter;
- $x$  — The variable;
- $F$  — Failure probability/%.

The corresponding reliability function  $R(x)$  can be expressed as:

$$R(x) = 1 - F(x) = \exp \left\{ - \left( \frac{x}{\alpha} \right)^\beta \right\} \quad (2-2)$$

The logarithm of both sides of the equation is taken twice to obtain the following formula (2-3) :

$$\ln(-\ln(1 - F(x))) = \beta(\ln x - \ln a) \quad (2-3)$$

If  $\ln(-\ln(1 - F(x)))$  is substituted by  $y$  and  $\ln x$  substituted by  $t$ , the Formula(2-4).

$$y = \beta(t - \ln a) \quad (2-4)$$

This transformation is called Weibull transform  $t$ - $y$  coordinates of the graphics for the Weibull probability distribution (Weibull Plotting Paper, WPP). In general, the  $y$ -axis displays the corresponding value of  $F(x)$  and the shape parameter is estimated based on the slope of the line. According to Formula (2-1), it can be seen that when the value of the variable  $x$  is equal to the scale parameter, no matter what the shape parameter is, the failure probability  $F(x) = 1 - e^{-1}$  is defined as the variable value when the failure probability is 63.2%. When analyzing the DC breakdown strength data of polyimide film samples, the scale parameter is used to represent the characteristic breakdown strength, which represents the breakdown strength when the sample failure probability is 63.2%. The shape parameter represents the

dispersion of the data. The larger the value is, the less the experimental data is dispersed.

The sample to be tested was cut into a round sample with a diameter of 30mm. After ultrasonic cleaning and drying, the upper and lower surfaces of the round sample were sprayed with gold. Test thermal stimulation current with NovoCONTROLLER Concept 90 TSDC test system with sample clipped by electrode whose diameter is 25 mm. The selected test conditions are shown in Fig. 2-5, where the polarization temperature is 160°C, the polarization time is 10 min, the polarization voltage is 250V DC, the test temperature is 100°C~200°C, and the rising rate of temperature is 2°C/min.

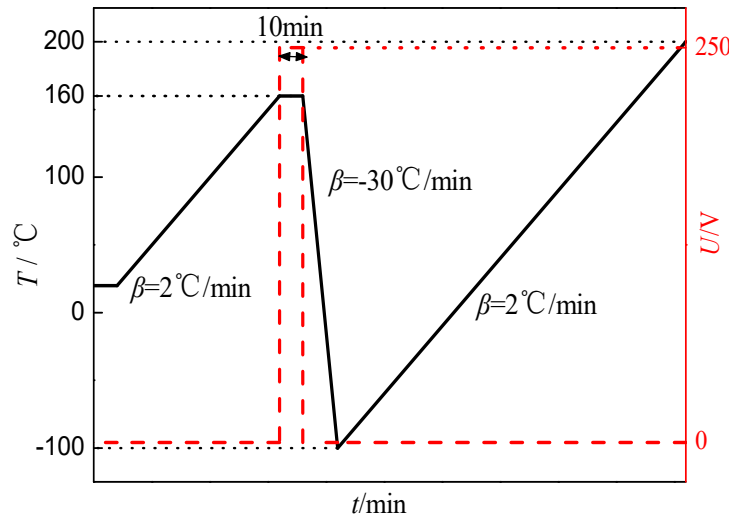


Fig. 25 Thermal stimulation current test conditions2-

Thermally Stimulated Depolarization (TSDC or TSC) is the short-circuit current detected at both ends of the electrode when the polarization process is completed within the dielectric material or when the depolarization process is completed when it is heated. The method is to hold the sample with two electrodes, and the carrier in the temperatured sample can be excited by obtaining energy. At this time, a DC voltage is applied to make each polarization process in the dielectric material fully completed. At this time, the carrier will drift to the electrode, and the internal dipole will be fully oriented. The temperature of the sample is then lowered so rapidly that the depolarization process is not completed and the carriers or dipoles inside the dielectric are "frozen". The TSDC curve is obtained by collecting and recording the relationship between the depolarization current of the short circuit of the galvanometer and the temperature at a fixed heating rate.

According to the thermal stimulation current theory, the TSDC experimental curve of a single relaxation process can be expressed by Formula (2-5) :

$$I_{TSC}(T) = \frac{p}{\tau_0} \exp \left[ -\frac{E_T}{kT} - \frac{1}{\beta \tau_0} \int_{T_0}^T \exp\left(-\frac{E_T}{kT}\right) dT \right] \quad (2-5)$$

Where:

$I_{TSC}$  -- Thermal stimulation current /A;

$p$  -- Polarization intensity / $C \cdot m^{-2}$ ;

$\tau_0$  -- The relaxation time constant /s;

$E_T$  -- Activation energy/eV;

$k$  -- Boltzmann constant, whose value is  $1.38 \times 10^{-23}$  J/K

$\beta$  -- Heating rate / $^{\circ}C \cdot min^{-1}$ 。

Generally speaking, the polymer dielectric must not only concentrate on relaxation polarization, but also contain several relaxation processes simultaneously, each of which corresponds to different polarization intensity  $p$ , relaxation time constant  $\tau_0$  and activation energy  $E_T$ . The thermal stimulation current of each relaxation process is governed by Formula (2-5), so in fact, the dielectric thermal stimulation current can be summed up with several relaxation processes with different parameters ( $p$ ,  $\tau_0$ ,  $E_T$ ), which is also called the Total Current Formula. The fitting parameters of polarization intensity, relaxation time and activation energy of each relaxation process can be obtained after programming the formula using Matlab. Combined with the parameters, the thermal stimulation current curve of polyimide film sample can be further analyzed to obtain the relevant information of dipole or moving ion in the testing medium.

All the test instruments and models used in this paper for performance testing of polyimide film samples are shown in Table 2-4. Nitrogen gas has been introduced during the experimental preparation process. First, the polyamic acid solution will also be hydrolyzed. The reason is that the amide group in the polyamic acid will spontaneously catalytically cleave, and the resulting anhydride will be due to the presence of moisture in the solvent (dianhydride and the water generated during the reaction of the diamine monomer in the flask) is hydrolyzed, so that the anhydride can no longer react with the amine to regenerate the amide; on the other hand, the nitrogen flow takes away water and will result in the polycondensation reaction proceeding in the positive direction and increasing the molecular weight of the polyamic acid produced by the reaction to achieve the ultimate goal of increasing the molecular weight of the polyimide sample. When the molecular weight of the synthesized polyamic acid is not large enough, the film forming property is greatly affected, in the second step of thermal imidization of the case where the film will be prone to fragmentate, so this step and standards for increasing the molecular weight of polyamic acid is crucial.

Table 2-3 Dianhydride monomer and solvent used in this paper2-

Table 2-4 Test equipment2-

Device name	Model
Spray konica minolta	Q150T
Infrared spectrometer	IRpresitge - 21
Differential calorimeter scanner	METTLER TOLEDO DSC 822E
Thermogravimetric analyzer	A TGA/SDTA851
Wideband dielectric spectrometer	Novocontrol Concept 80
Thermal stimulation current testing system	Novocontroller Concept 90 TSDC
Breakdown experimental system	BDJC - 100 kV

In this chapter, the experimental method of synthesizing polyimide films by dihydride and diamine monomer is established, and a platform for the preparation of polyimide film sample is built in the laboratory. This chapter also introduces the relevant information of the selected monomers and reagents used in the preparation of polyimide films in this paper, as well as the preparation equipment and process of polyimide films in detail. Finally, it introduces the experimental conditions and equipment of thermal performance test and energy storage performance test.

### 3 STUDY ON THE INFLUENCE ON THE ENERGY STORAGE CHARACTERISTICS OF DIFFERENT MAIN CHAIN STRUCTURES OF POLYIMIDE FILM

In order to compare the influence of different main chain structure of polyimide on energy storage characteristics, in this chapter three different diamine monomers, which are 4,4'-oxydianiline, 4,4'-(1,3-Phenylenedioxy)dianiline, 3,3'-(1,3-phenylenebis(oxy))dianiline, and two different dianhydride monomers, which are 1,2,4,5-Benzenetetracarboxylic anhydride and 3,3',4,4'-Biphenyltetracarboxylic dianhydride, are selected to synthesize the four different polyimide film with different main chain structure according to the method and process mentioned in the second chapter and all of the samples are pretreated. This chapter mainly introduces the four polyimide film samples with different main chain structure, their structure characterization and their performance test results. The result of the tests are compared and the influence on the thermal properties, breakdown voltage and dielectric properties of polyimide film are analyzed when the monomer in the main chain of rigid conjugate structure (PCB), introduction of flexible structure unit (ether bond) and change the position of amino in diamine part on the benzene ring.

By changing the main chain structure of the aromatic polyimide, for example, introducing a sulfur atom, introducing an ether bond or introducing a non-coplanar twisted structure into the monomer main chain, etc., the degree of twisting of the polyimide molecular chain can be changed, which affects the large  $\pi$  bond system formed by the benzene ring and the five-membered imide ring between the polyimide segments, changes the close packing structure of the molecular chain and affects the dielectric properties and thermal properties of the polyimide. The molecular structure design, synthesis and utilization of novel aromatic polyimide materials can be accomplished by selecting different dianhydride and diamine monomers with different monomer structures, and the main chain structure of polyimide materials also can be controlled by the same method. Most existing research usually focuses on the influence on the optical properties, solubility properties, and thermal properties of polyimide materials brought by structural changes. Some studies involving dielectric constants are mainly based on reducing dielectric constants as interlayer insulation of electronic devices. Mainly, there are not many studies on the effect of structural changes on energy storage characteristics, and there is a lack of comprehensive research on the effect of structural changes on energy storage characteristics from the side of dielectric constant and breakdown strength.

Fig. 3-1 (a) ~ (e) is the molecular structure of dianhydride and diamine monomer selected to synthetic polyimide sample in this section, they are 1,2,4,5-Benzenetetracarboxylic anhydride and 3,3',4,4'-Biphenyltetracarboxylic dianhydride, 4,4'-oxydianiline, 4,4'-(1,3-Phenylenedioxy)dianiline and 3,3'-(1,3-phenylenebis(oxy))dianiline. The structure of each

monomer and their corresponding name of the abbreviation as shown in Fig. 3-1. For the convenience to show and explain, the abbreviations of samples are used in this work instead of full name. In this section, the most typical polyimide, Kapton structure (PMDA-ODA) is selected, and on this basis, three kinds of polyimides containing biphenyl structures are synthesized by changing the structure of dihydride monomer, hoping to obtain polyimides with greater breakdown strength on the premise of maintaining good thermal properties. Compared with PMDA, the difference between BPDA and PMDA lies only in the introduction of biphenyl, and the flexible decline of molecular chain after the introduction of biphenyl usually leads to the decrease of film-forming property. To make up for this, an ether bond is introduced on the basis of ODA to obtain the diamine monomer TRDA. At the same time, in order to further study the influence of spatial structure change on polyimide energy storage density, TMDA, an isomer of TRDA, was selected. The difference lies in the substitution position of amino group on the benzene ring, the former is para substitution and the latter is interposition substitution.

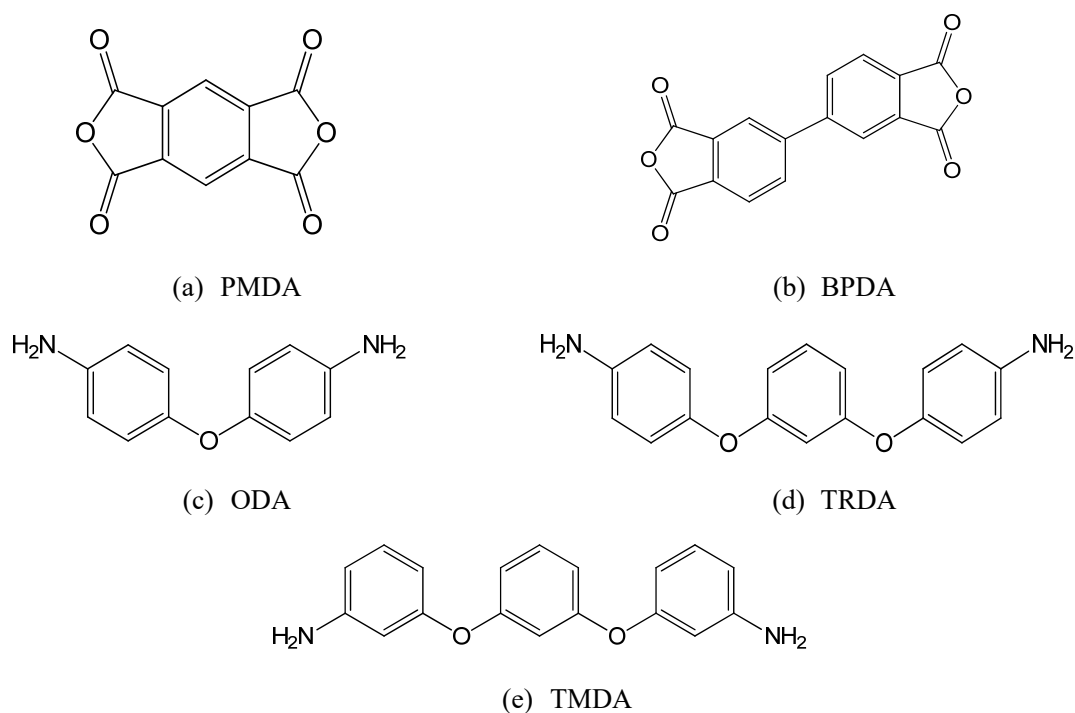


Fig. 3-1 Molecular structures of diamine and dianhydride monomers<sup>31</sup>

Fig. 3-2 (a)~(d) is the molecular structure of four polyimide samples with different structures synthesized by using the five monomers above, which are PMDA-ODA, BPDA-ODA, BPDA-TRDA and BPDA-TMDA in sequence. The names are composed of the abbreviation of dihydride and diamine of the synthetic sample connected by hyphen, for example, sample PMDA-ODA is synthesized from 4,4'-oxydianiline (ODA) and 1,2,4,5-Benzenetetracarboxylic anhydride (PMDA), sample BPDA-ODA is synthesized from 4,4'-oxydianiline (ODA) and 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), and sample BPDA-TMDA is synthesized from 3,3'-(1,3-phenylenebis(oxy))dianiline (TMDA) and 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA). Sample BPDA-TRDA was synthesized



from 4,4'-(1,3-Phenylenedioxy)dianiline (TRDA) and 3,3',4,4'-Biphenyltetracarboxylic dianhydride anhydride (BPDA).

Fig. 3-3(a)~(d) is the spatial structure diagram of the four polyimide film samples above with different main chain structures optimized by ChemBio3D Ultra software via MM2 according to the minimum energy principle. In the schematic ball model, the gray sphere represents carbon atoms, the blue sphere represents nitrogen atoms, the red sphere represents oxygen atoms, the yellow sphere represents fluorine atoms, and the pink sphere represents isolated electron pairs. Comparing the four different structure of polyimide according to Fig. 3-2 and Fig. 3-3, BPDA-ODA have one more biphenyl structure compared with PMDA-ODA, which makes the dianhydride have a bigger conjugate structure rigidity. Sample BPDA-TRDA have one more ether bond in diamine part than sample BPDA-ODA, which increased the molecular chain of kindness. Most of the existing research shows that the introduction of the ether bond can reduce the dielectric constant, but the influence on the breakdown voltage and the energy storage density is still worth exploring. Comparing BPDA - TMDA with BPDA - TRDA, the difference lies in the substitution position of amino group on the benzene ring, the former is para substitution and the latter is interposition substitution which causes bigger space steric effect to the molecular chain caused by of rigid conjugate structure in dianhydride part and makes the molecular chain relatively more curved. It can be found in Fig. 3-3 that the space structure of BPDA - TMDA is more distorted so that the rotation of ether bond is impeded to a certain extent and the flexibility of molecular chain is lower thanr BPDA - TRDA.

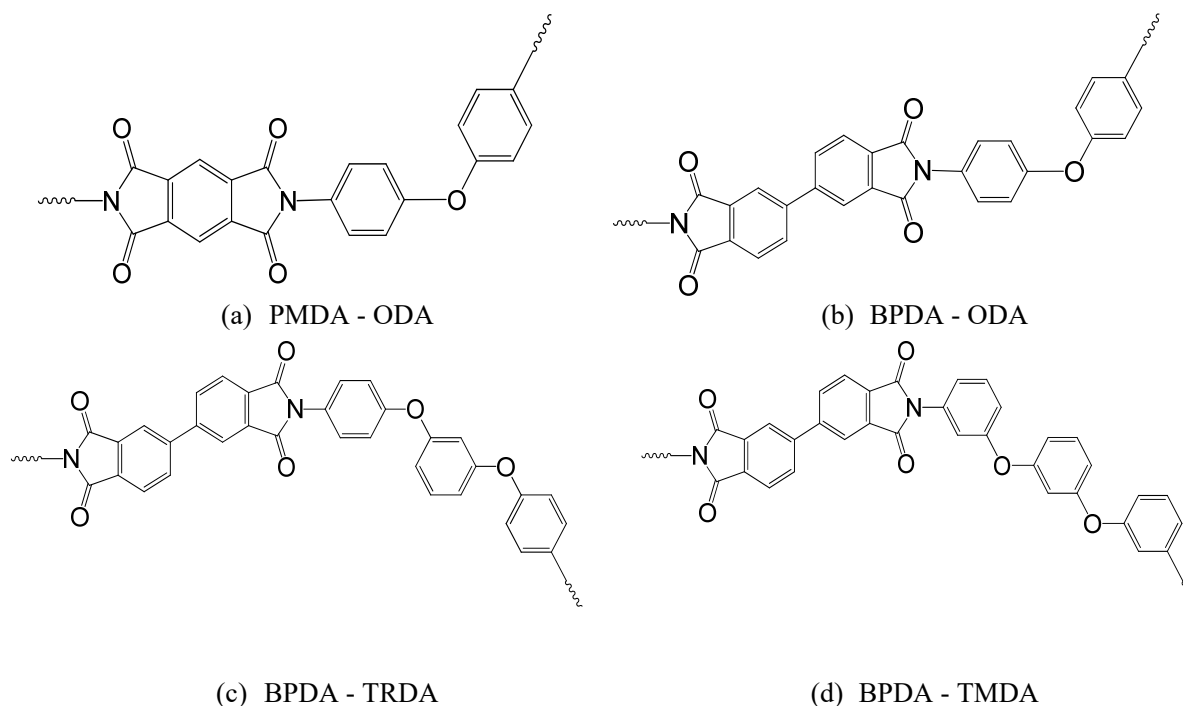


Fig. 3-2 Polyimides with different mainchain structures3

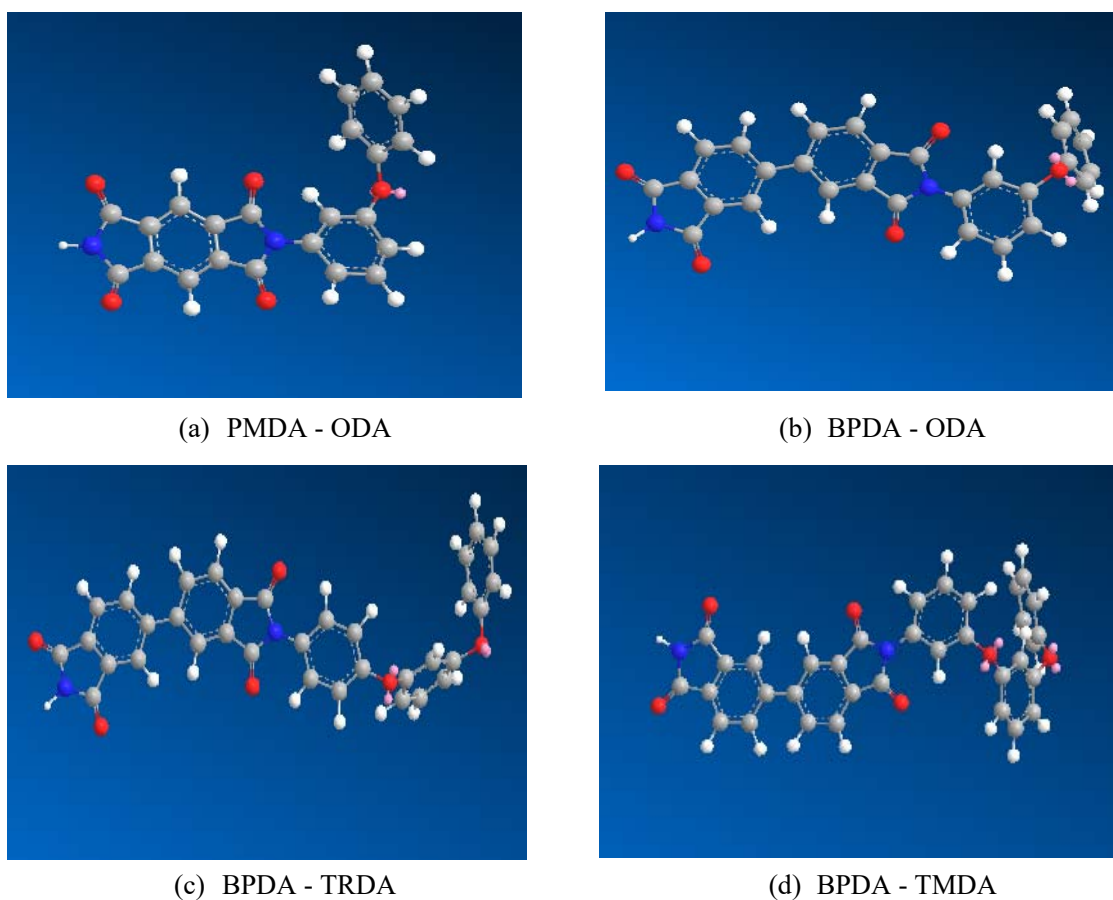


Fig. 3-3 Molecular spatial configurations of polyimides with different mainchain structures3-

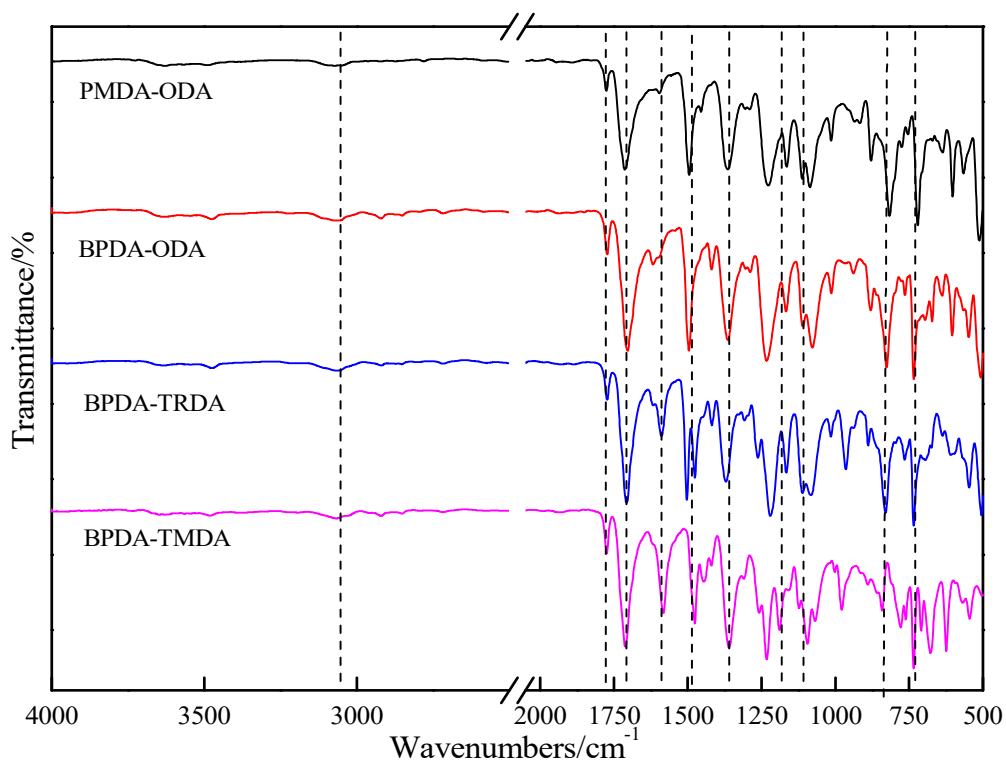


Fig. 3-4 FT-IR of polyimide film samples with different mainchain structures3-

Table 3-1 FT-IR analysis of polyimide film samples with different mainchain structures

The name of samples	Imide band I	Imide band II	Imide band III	Imide band IV	Aromatic ether	Polysubstituted benzene surface External bending vibration	Vibration of the bone of benzene ring	C - H vibration on benzene ring	Deformation and vibration of imide ring
PMDA - ODA	1777	1710	1365	720	1226	817	1596, 1495, 1453	3073	1087
BPDA - ODA	1774	1702	1363	735	1233	825	1601, 1496, 1460	3069	1078
BPDA - TRDA	1774	1711	1360	735	1232	840	1582, 1492, 1449	3065	1067
BPDA - TMDA	1773	1706	1369	735	1220	830	1589, 1503, 1450	3058	1078

Each molecule has a unique chemical composition and molecular structure, under infrared radiation with continuous wavelength, the molecules will be selectively absorb certain wavelengths of infrared ray, this is because the molecular internal functional groups and chemical bond rotation and vibration of the advantage of this phenomenon. FT-IR analysis can be used to analyze the molecular rotation and vibration and then qualitative identificate the material by the characteristics of the structure and chemical composition of the testing material. The structural characterization of the four polyimide film samples prepared in this section were achieved by FT-IR and the spectrum is shown in Fig. 3-4. The ordinate is the percentage transmittance (%) and the abscissa is the wave number ( $\text{cm}^{-1}$ ). The characteristic spectral peak of each sample is shown in Table 3-1.

Taking the FT-IR spectrum of PMDA-ODA as an example, the location and attribution of the bands of polyimide film samples were introduced as following. There is a =CH stretching vibration peak on the benzene ring between  $3000 \text{ cm}^{-1} \sim 3100 \text{ cm}^{-1}$ . Characteristic peaks of imide ring can be observed near  $1778 \text{ cm}^{-1}$  and  $1713 \text{ cm}^{-1}$  respectively. They represent symmetric (or in-phase) and asymmetric (or inverse-phase) stretching vibration peaks of carbonyl C=O on the pentameter ring, which are called imide band I and imide band II respectively. The C-N stretching vibration peak on the imide ring, also known as the imide band III, was observed near  $1369 \text{ cm}^{-1}$ . The peak at  $1110 \text{ cm}^{-1}$  and  $735 \text{ cm}^{-1}$  represents the deformation vibration of imide ring, which is the variable angle vibration of C=O, and the latter is also called imide band IV. The appearance of imide band I, band II, band III and band IV indicates that the product species contains imide rings. The three peaks observed near  $1590 \text{ cm}^{-1}$ ,  $1496 \text{ cm}^{-1}$ , and  $1453 \text{ cm}^{-1}$  are absorption peaks of typical benzene ring skeleton stretching vibration, and those near  $840 \text{ cm}^{-1}$  are absorption peaks of polysubstituted benzene ring bending vibration, indicating that the product contains polysubstituted benzene rings. Stretching vibration peak of aromatic interring ether bond -O- was observed near  $1271 \text{ cm}^{-1}$ , indicating the presence of aromatic ether in the sample. No typical vibration absorption peak of amino group was found within  $3200 \text{ cm}^{-1} \sim 3500 \text{ cm}^{-1}$ , indicating that there was no polyamide acid in the sample. In conclusion, the product is aromatic polyimide with ether bond and the polyamide acid is completely converted into polyimide in the process of thermal imidatio, which proves that the polyimide film with target structure is obtained. The analysis of BPDA-ODA, BPDA-TMDA and BPDA-TRDA is similar to that of PMDA-ODA.

Fig. 3-5 is the TGA curve of PMDA-ODA, BPDA-ODA, BPDA-TRDA and BPDA-TMDA prepared in this chapter, which is tested by thermo gravimetric analyzer in the nitrogen flow. The  $x$ -axis is the temperature, the range is 50-900 °C, and the  $y$ -axis is the weight percentage. The rising rate of temperature is 10°C/min. The thermal performance parameters of PMDA-ODA, BPDA-ODA, BPDA-TMDA and BPDA-FBDA polyimide films is listed in Table 3-2. Where  $T_{d10}$  is the temperature at 10% weight loss,  $T_s$  is the initial decomposition temperature,  $T_d$  is the temperature where the maximum decomposition rate located. Char Yield is the percentage of sample residual weight at 900°C.

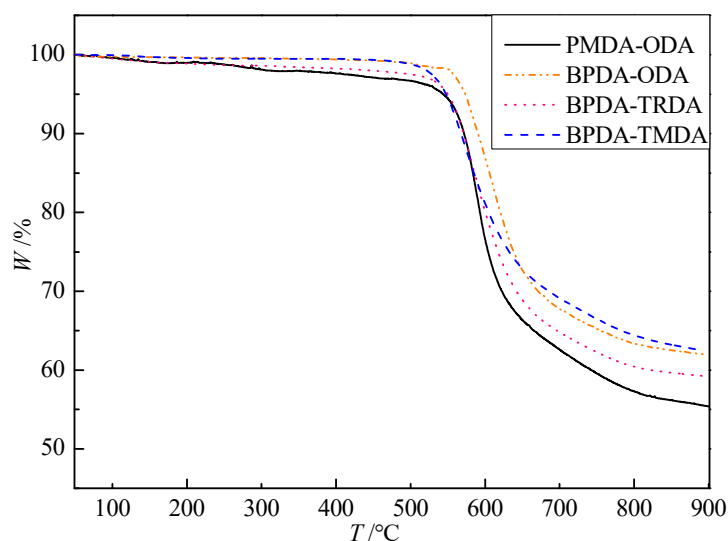


Fig. 35 TGA curves of polyimide film samples with different main chain structures3-

According to Fig. 3-5 and Table 3-2, it can be found that the initial decomposition temperature range and 10% weight loss temperature range of the four polyimide film with different main chain structure are in 535-552 °C and 571-591 °C separately. The result shows that this kind of aromatic polyimide has excellent thermal stability, which is due to the existence of the rigid structure of benzene ring main chain that makes the molecular chain not easy to fracture under heating thus the thermal decomposition of materials are more difficult. Due to the high content of benzene rings in the molecular framework, the carbon residue rates of the four samples were all high, above 55% at 900°C.

The  $T_s$  of PMDA-ODA was lower than that of BPDA-ODA, because the biphenyl in the molecular chain skeleton structure increased the thermal stability of the molecular chain. However, the  $T_s$  of BPDA-TRDA is slightly lower than that of BPDA-ODA because after the introduction of ether bond in dianhydride, the molecular chain of synthesized polyimide has a larger rotation range when subjected to thermal motion and the molecular chain is more likely to break at the ether bond, so its thermal stability is relatively reduced. The  $T_s$  of BPDA-TMDA is slightly higher than that of BPDA-TRDA. Due to the change of the substitution of amino group, the steric hindrance effect of conjugated structure with the large volume on the dihydride increases, hindering the rotation of the ether bond and thus making the thermal stability relatively higher. The thermal stability of polyimide was slightly improved

when the rigid conjugated structure (such as biphenyl) was added to the dihydride, while the thermal stability of polyimide was slightly decreased when biphenyl was added to the molecular backbone, ether bond was introduced into the dihydride part or the substitution position of on the benzene ring was changed.

Table 3-2 Thermal properties of polyimide film samples with different mainchain structures

The sample name	10% weight loss temperature Td/ $^{\circ}$ C <sub>10</sub>	Initial decomposition temperature Ts/ $^{\circ}$ C	Maximum decomposition rate temperature Td/ $^{\circ}$ C	Carbon residue rate / %	Glass transition temperature Tg/ $^{\circ}$ C
PMDA - ODA	571.14	542.39	593.83	55.46	188.93
BPDA - ODA	590.55	552.89	607.67	61.93	255.23
BPDA - TRDA	571.37	535.08	569.04	67.34	243.52
BPDA - TMDA	571.36	544.91	581.18	59.23	252.53

DSC curves of the samples was tested by Differential Scanning Calorimetry under nitrogen protection and the rising rate of temperature is 10 $^{\circ}$ C/min. Fig. 3-6 shows the DSC curves of polyimide films with four different main chain structures. The *x*-axis is the temperature, the unit is  $^{\circ}$ C, the *y*-axis is the enthalpy change and the unit is W/g. The steps in the curve represent the Glass transition process. As shown in Fig. 3-6, the Glass transition temperatures of the four polyimides were all above 188  $^{\circ}$ C, indicating that the thermal properties of the four polyimides samples were all outstanding, and they had obvious advantages over other polymer materials when used at relatively high temperatures.

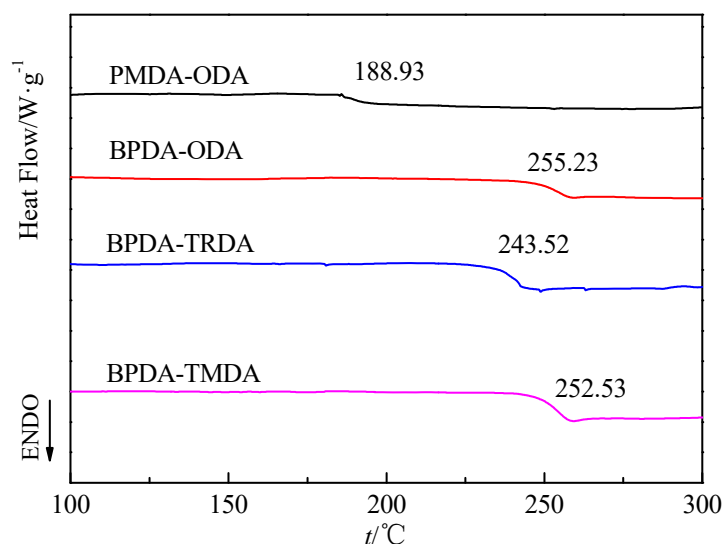


Fig. 3-6 DSC curves of polyimide film samples with different main chain structure3-

The difference of glass transition temperature of polyimide is usually caused by the degree of entanglement of polymer chain and the density of accumulation. The *T<sub>g</sub>* of three kinds of polyimide film sample synthesized using BPDA is obviously higher compared to PMDA - ODA, this is because rigid larger biphenyl molecular skeleton structure is introduced into BPDA compared to PMDA, which results in the decrease of polyimide main chain of the

flexible. At the same time, biphenyl imide ring and carbonyl formation of big conjugate structure is conducive to the formation of CTC, which increases the degree of close packing of the molecular chains, and the resistance in relative motion between molecular chains increased thus the  $T_g$  is higher.  $T_g$  of BPDA-TRDA is slightly lower than that of BPDA-ODA, because TRDA introduces more flexible ether bonds that can be rotated, which increases the flexibility of the molecular chain, and thus  $T_g$  decreases. Compared with BPDA-TRDA, BPDA-TMDA has a large steric hindrance effect when compared with contralateral substituted diamines. The molecular chain rigidity increases and the degree of molecular chain distortion and winding increases thus  $T_g$  is higher.

In this section, the Concept 80 broadband dielectric spectrometer is used to measure the broadband dielectric spectra of four polyimide film samples prepared with different main chain structures. The measurement temperature range is  $20^\circ\text{C} \sim 200^\circ\text{C}$ . The frequency is  $10^2 \text{ Hz} \sim 10^6 \text{ Hz}$ . The polarization process and dielectric loss of the polyimide film in the measurement temperature range are studied through the analysis of the relative dielectric constant spectrum and the dielectric loss tangent spectrum, so as to further discuss the influence of different main chain structures on the dielectric properties of polyimide films.

Fig. 3-7 (a) ~ (d) shows the relative permittivity spectrum of PMDA-ODA, BPDA-ODA, BPDA-TRDA and BPDA-TMDA respectively. The ordinate is the relative permittivity, the x-axis coordinate is the logarithm of frequency, and Fig. 3-8 is the imaginary part of the complex permittivity of PMDA-ODA. Table 3-3 shows the relative dielectric constant and tangent of dielectric loss Angle of polyimide film samples measured at  $20^\circ\text{C}$  and 50 Hz, as well as the electric saving dipole moments of each chain calculated after MM2 optimization in ChemBio3D Ultra.

According to formula (3-1) Frohlich model,  $\epsilon_r \propto Ngu^2$ , in other words, the dielectric constant of the material can be increased by increasing the packing density of the molecular chain, decreasing the free volume to increase the electric dipole density  $N$  or increase the electric dipole moment  $u$ .<sup>[59-61]</sup>

$$\frac{(\epsilon_{rs} - \epsilon_{r\infty})(2\epsilon_{rs} + \epsilon_{r\infty})}{\epsilon_{rs}(\epsilon_{r\infty} + 2)^2} = \frac{Ngu^2}{9\epsilon_0 kT} \quad (3, 1)$$

where:

$\epsilon_{rs}$ 、 $\epsilon_{r\infty}$ 、 $\epsilon_0$  ——The relative permittivity, optical frequency permittivity and vacuum permittivity are respectively.

$N$ ——Electric dipole density / $\text{m}^{-3}$ ;

$\mu$ ——electric dipole moment / $\text{C}\cdot\text{m}$ ;

$k$ ——Boltzmann constant, size  $1.38 \times 10^{-23} \text{ J/K}$ ;

$T$ ——temperature / $^\circ\text{C}$ ;

$g$ ——Correlation factors related to intermolecular forces.

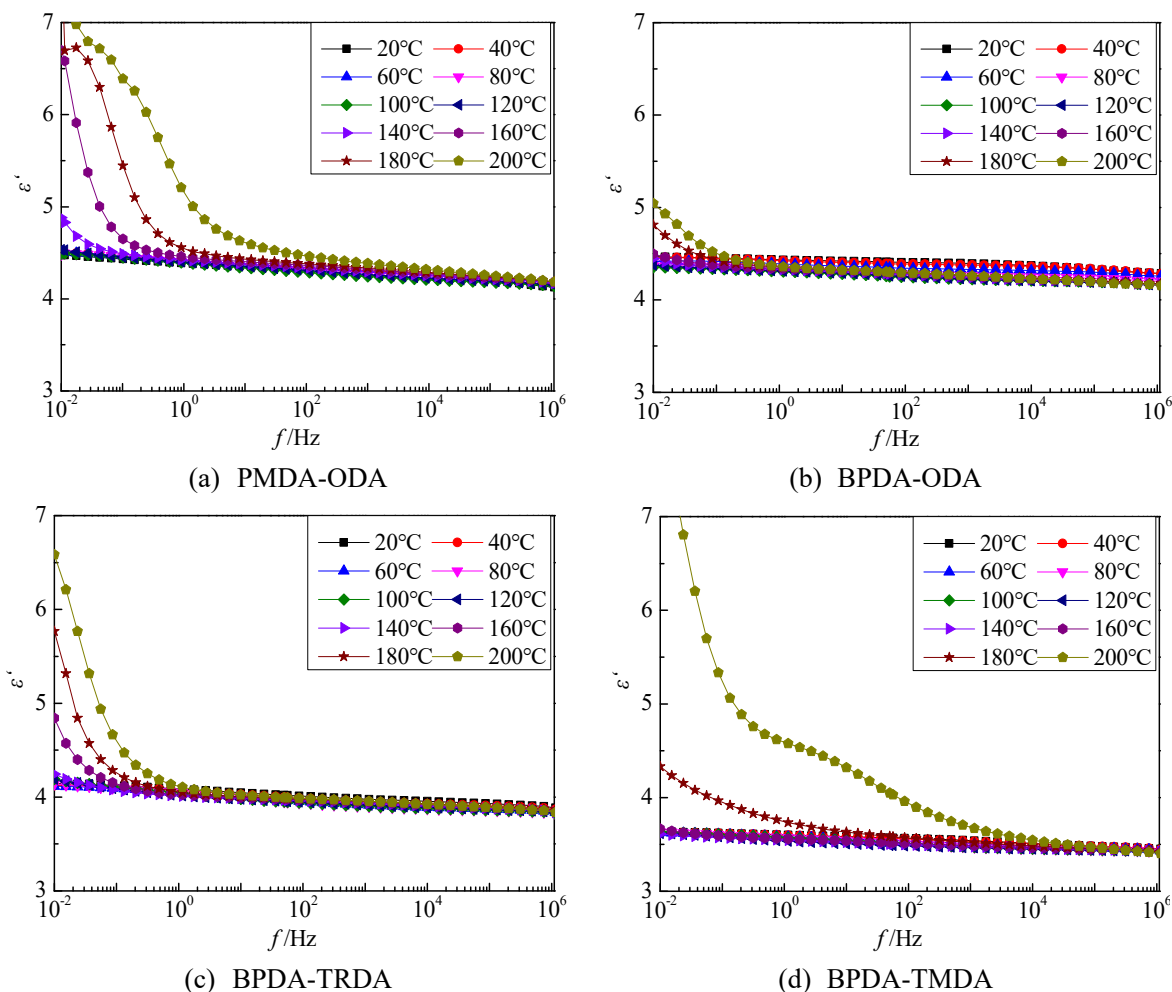


Fig. 3-7 Dielectric constant spectroscopy of polyimide film samples with different main chain structures

According to Fig. 3-7, for the four polyimide film samples prepared in this chapter, the dielectric constant, except for the step at high temperature (higher than 160 °C) and low frequency, basically presents a slightly decreasing trend with the increase of frequency. Taking PMDA-ODA as an example, the relative dielectric constant at 20 °C ranges from 3.99~4.47 (10<sup>-2</sup> Hz ~10<sup>6</sup> Hz), showing that the prepared polyimide film samples have high dielectric stability, with little variation with frequency and temperature. As can be seen from Fig. 3-7, the relative dielectric constant of BPDA- ODA, BPDA-TRDA and BPDA-TMDA changes little with temperature, and the dielectric stability is good. Only at high temperature and low frequency increased sharply with the increase of temperature, and the amplitude was smaller than that of PMDA-ODA, which indicated that the introduction of biphenyl structure in the main chain structure was beneficial to improve the dielectric stability of polyimide materials.

The relative dielectric constant of sample BPDA-ODA is higher than that of PMDA-ODA, which is due to the presence of conjugate biphenyl structure in the dianhydride. It help to form a larger charge transfer complex (CTC), which increases the electric dipole moment of the dipole (a chain node as a whole is regarded as an electric dipole), which conforms to the calculation results of the electric dipole moment in Table 3-3. The comparison between BPDA-ODA and BPDA-TRDA shows that the introduction of ether bond on diamine increases

the flexibility of polyimide molecular chain and the free volume in the material, and makes the relative dielectric constant slightly decreased. Compared with BPDA-TRDA, the relative dielectric constant of BPDA-TMDA is further reduced because the change of substitution of the amino group on diamine on the benzene ring causes the molecular chain to be extremely twisted, the close packing between the molecular chains is destroyed and large free volume is generated in the material, thus further reducing the relative dielectric constant.

Table 3-3 Relative dielectric constant and tangent of dielectric loss Angle of polyimide film samples with different main chain structure

The sample name	PMDA - ODA	BPDA - ODA	BPDA - TMDA	BPDA - TRDA
Debye chain saving dipole moment	2.337	3.225	3.107	3.228
Relative dielectric constant	4.33	4.57	3.57	4.02
Tangent tangent delta of the dielectric loss Angle $(10)^{-3}$	4.86	1.79	6.17	3.78

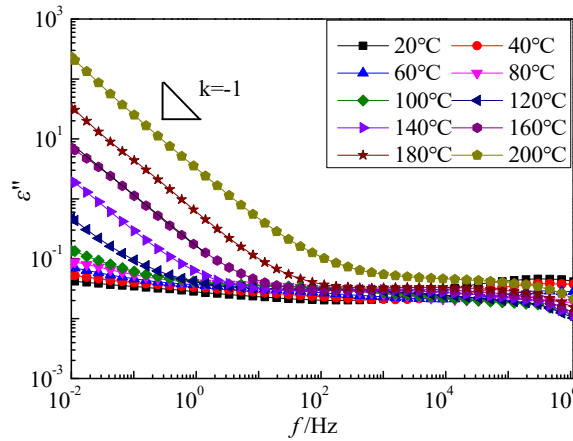


Fig. 3-8 Virtual part spectrum of complex dielectric constant of sample PMDA-ODA3-

Fig. 3-9 (a) ~ (d) shows the loss spectroscopy of PMDA-ODA, BPDA-ODA, BPDA-TRDA and BPDA-TMDA respectively. According to Table 3-3, the dielectric loss of the four polyimide films are all smaller than the order of  $10^{-3}$ , indicating that polyimide materials have the advantages of small energy loss and high energy conversion rate as energy storage materials.



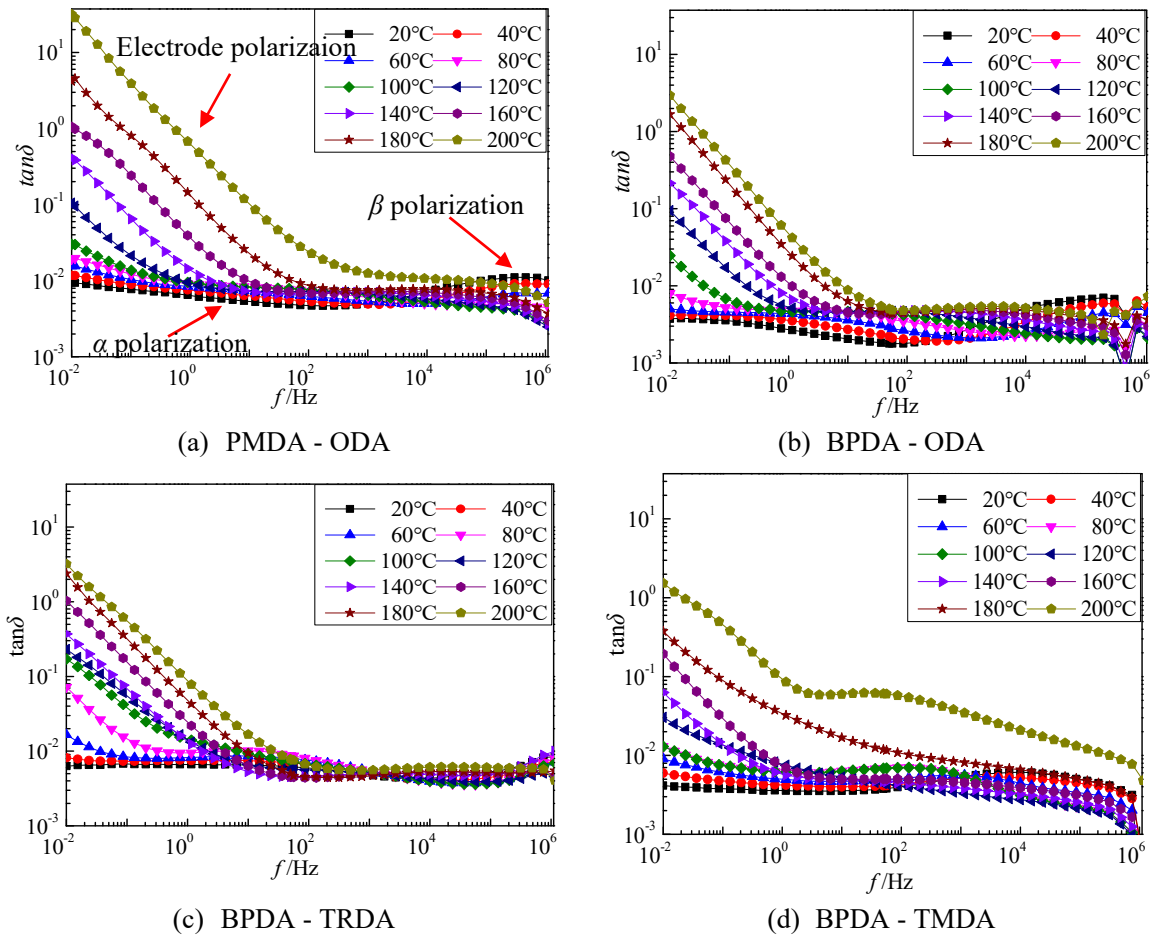


Fig. 3-9 Dielectric loss spectroscopy of polyimide film samples with different mainchain structures3-

Taking PMDA-ODA as an example to introduce the loss spectroscopy of PI films. It can be seen that there are three polarization processes in PI films in Fig. 3-9(a). Among them, the conductivity loss caused by electrode polarization is shown at high temperature and low frequency. This can be proved by that the slope of the imaginary part of the complex dielectric constant at the corresponding frequency at the log-log coordinate is -1 in Fig. 3-8.<sup>[60]</sup> A second loss peak can be seen at frequencies slightly above the electrode polarization, which is caused by the motion of the molecular chains., because of the large polyimide molecular weight of the main chain of the molecule movement ability is weak, the polarization process occurred in low frequency band (usually  $< 10^4$  Hz), and when the temperature rises, the polarization peak moves toward high frequency, it is because the molecular thermal motion increases with the increase of temperature, is advantageous to the molecular chain orientation in the electric field, dielectric relaxation process faster. A third loss peak can be seen at low temperature and high frequency ( $> 10^4$  Hz). This loss peak is attributed to the polarization process caused by the turning of the dipole group (C=O, C-O, and C-N groups). Fig. 3-10 (a) ~ (d) respectively shows the polarization process of polyimide film samples with four different main chain structures, PMDA-ODA, BPDA-ODA, BPDA-TRDA and BPDA-TMDA Its ordinate is linear coordinate and focuses on the polarization process at low temperature and high frequency (below  $100^\circ\text{C}$  and above 10 Hz).<sup>4</sup>

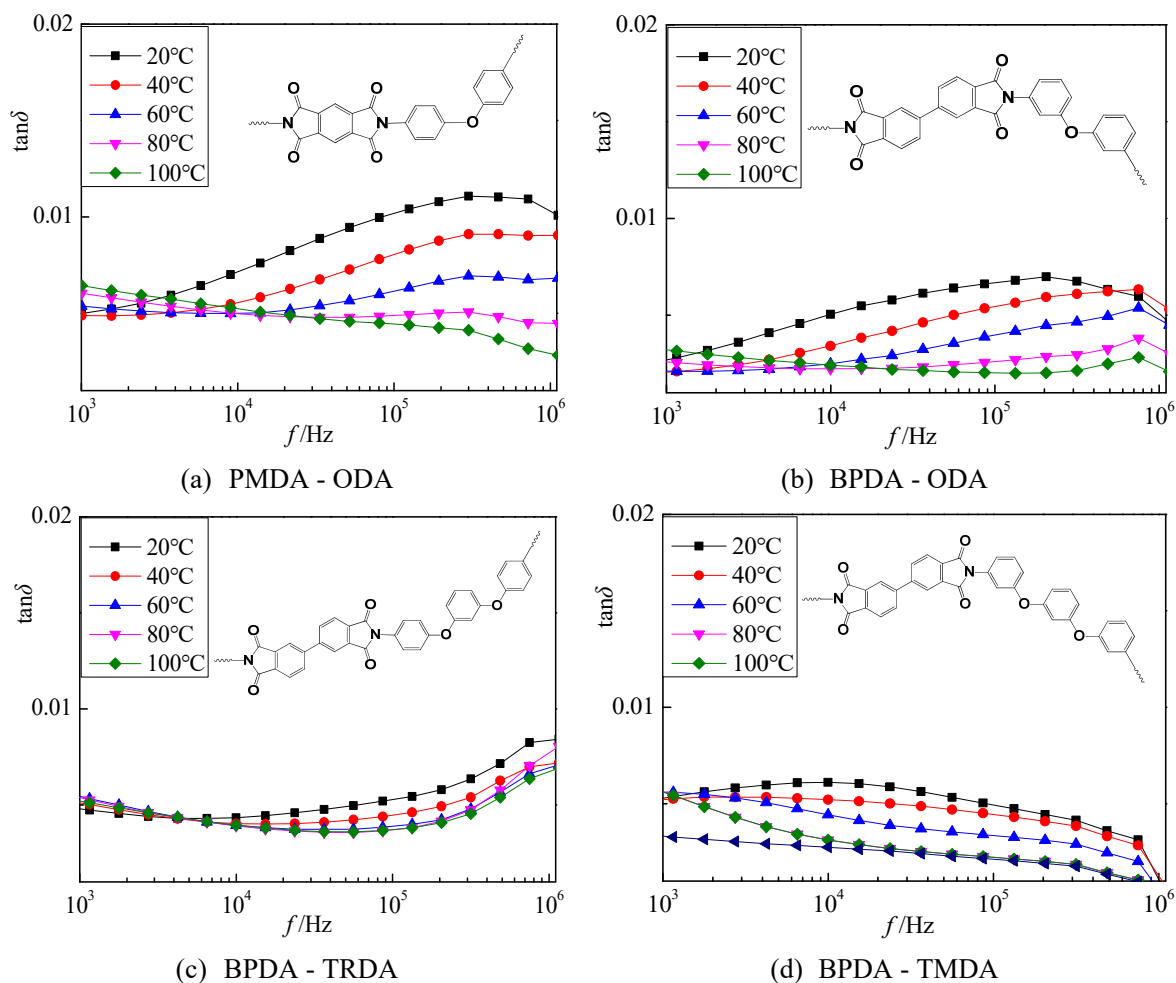


Fig. 3-10  $\beta$  polarization process of polyimide film samples with different mainchain structures3-

The loss spectroscopy of PMDA-ODA and sample BPDA-ODA is very similar, because they have similar structure and similar polarization process. The latter has lower dielectric loss because the introduction of benzene ring reduces the number of dipoles that can be oriented per unit volume. The polarization process of BPDA-TRDA is in a relatively low frequency band, because the introduction of ether bond increases the flexibility of the molecular chain, the motion range of the molecular chain is larger, and the influence of temperature is relatively small, and the relaxation time is longer. The polarization process of BPDA-TMDA is not obvious, and only occurs when the temperature is over 60°C. The steric hindrance effect brought by ortho substitution greatly obstructs the movement of molecular chains. Loss peak of  $\beta$  process of polarization is bigger in PMDA - ODA than in BPDA - ODA, the imide ring per unit volume and the former more about the amount of the group. And this is the reason why the peak of  $\beta$  process in BPDA - TMDA is lower than that of the first two because the introduction of the ether bond increases the molecular chain link and the free volume of material, and the number of groups per unit volume decrease in the sample. The  $\alpha$  process and the process are related to each other.  $\beta$  process of samples with obvious processes (e.g., BPDA-TRDA) are located in the higher frequency range because the movement of the molecular chain accelerates the orientation of the groups on the molecular chain.

In this paper, Origin software was used to achieve the two-parameter Weibull distribution failure probability graph of the breakdown strength of each sample, and the shape parameter and scale parameter were obtained. Blom method was used for scoring with a confidence interval of 95%. The shape parameter represents the dispersion of the data. The larger the shape parameter is, the smaller the dispersion of the sample data is. The scale parameter represents the breakdown strength of the measured material when the failure probability is 63.2% in weibull distribution. The unit is kV/mm, and it is used to represent the breakdown strength of the measured material. The breakdown vottage distribution diagram of PMDA-ODA, BPDA-ODA, BPDA-TRDA and BPDA-TMDA samples is shown in Fig.3-11 (a) ~ (d). The horizontal coordinate is the breakdown strength, and the unit is kV/mm.  $x$ -axis represents the probability of failure.

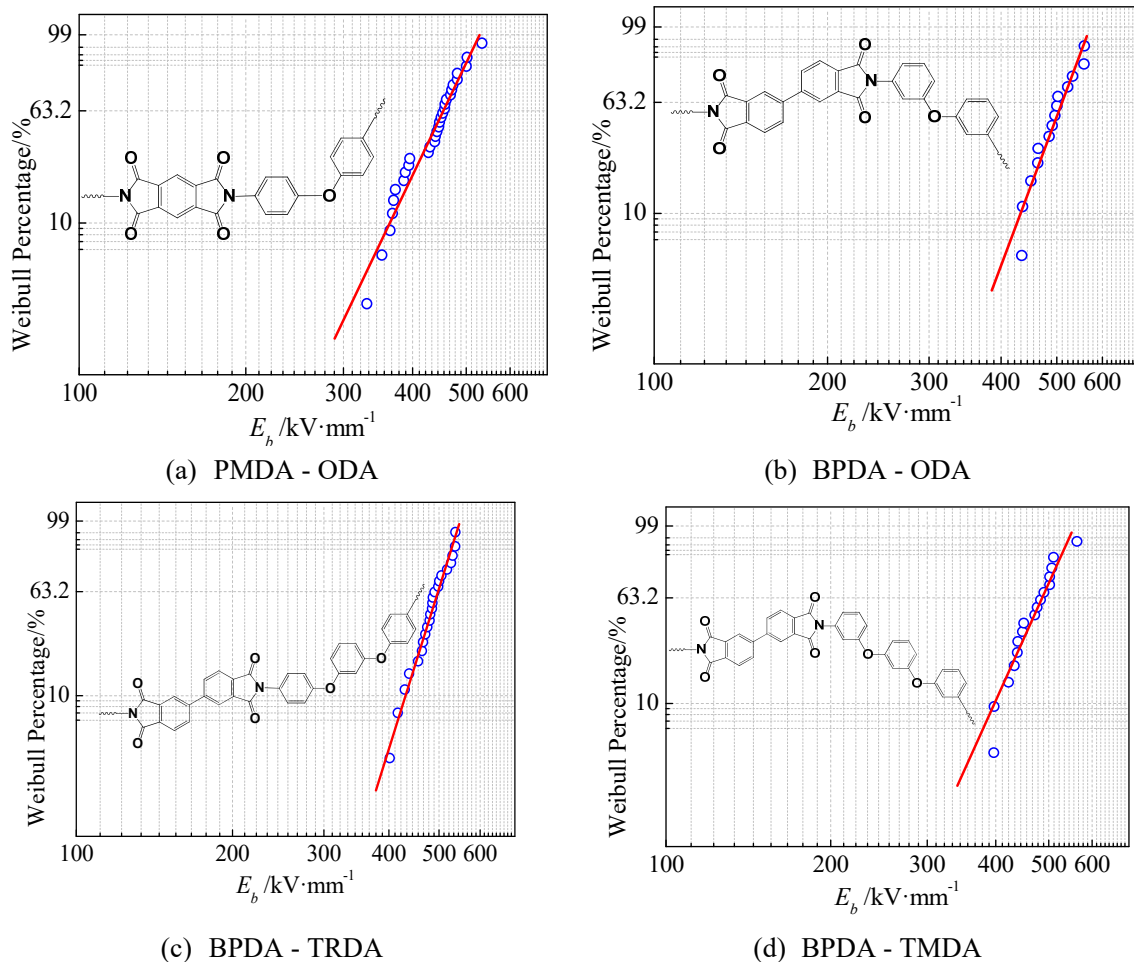


Fig.3-11 Weibull distribution of breakdown strength of PI samples with different mainchain structures

The phenomenon of electric breakdown of polymer is about the formation of high-energy electrons under strong electric field, resulting in constant collision ionization and finally doubling of the number of electrons. With the rapid increase of the number of free electrons, the conductivity reaches the stage of instability and the breakdown will occur, accompanied by the destruction of chemical structure. However, the end groups, twists and turns of the polymer chains and fractures will form electric charge traps. The interaction between these traps and electrons makes the traps not only the source of the formation of hot electrons, but

also the reaction of the chemical structure destruction of the sample, affecting the breakdown performance of the sample. Generally speaking, the DC breakdown strength of the polymer is related to many factors such as temperature, additives, sample thickness, internal deformation and crystallinity caused by different processes. It is showed in Chapter 3-2 that there is no melting peak in DSC curves of all the polyimide film samples indicates that the PI samples are in amorphous state. The high purity of monomers and same technology and thermal imidation process to synthesize and form the film ensure similar thickness of the samples, so the reasons of difference of breakdown voltage is mainly analyzed in this section from the perspect of difference of molecular structure and the possible different traps.

Table 3-4 shows the Weibull distribution parameters of the DC breakdown test of each polyimide film sample after processing data in Origin. It can be seen from the table that shape parameter of Weibull distribution of breakdown strength of each sample is above 10, indicating good dispersion of the experimental data. For the scale parameter, the breakdown strength of the four samples is generally higher than 454.5kV /mm, which indicates that the four polyimide samples obtained in this chapter have a high breakdown strength. And BPDA - ODA has the highest breakdown voltage that reaches to 510.8 kV/mm, it is higher than the breakdown strength of PMDA-ODA because biphenyl dianhydride is boosting the molecular chain rigidity of the structure and the existence of a large conjugated system makes close packing of the material increased, which also means less internal structure defects and less possibility to activate hot electron which makes the breakdown voltage is relatively higher. breakdown strengths of BPDA-ODA, BPDA-TRDA and BPDA-TMDA are all less than that of PMDA-ODA because the introduction of ether bond on diamine part makes the molecular chain more flexible, increases the molecular bending property and the free volume. As a result, free path for electron increases so that the probability of electrons getting accelerated under the external electric field and changing into high-speed electrons increases, so the breakdown strength of the polyimide film decreases. Compared with BPDA-TMDA, the high breakdown strength of BPDA-TRDA is due to the increase of steric hindrance effect of molecular chain caused by meta-position substitution instead of ortho-position substitution of amino, which affects the compact accumulation of molecular chain and the increase of free volume, thus reducing the breakdown strength.

Alagiriswamy A.A et al. applied TSDC experiments with different bias voltage and the conclusions are as following: for pure polyimide materials, the peak of TSDC curve appearing at lower temperature (around 270 K) represented the movement of the side group.<sup>[62]</sup> The peak appearing at near 400 K may be caused by the movement of the position of the lateral group or the carbonyl group. At this time, the lateral group or carbonyl group exists not only as natural dipole moment, but also as the trap center. The current peak near the higher temperature (440 K) is closely related to the relaxation process of space charge formed by carrier captured in the deep trap inside the material and is also related to the motion of molecular chains. Since the deep trap of the current peak reaction near 440 K is most related to the breakdown strength, the difference of the current peak near 440 K of each sample is mainly discussed in this paper. Four different polyimide film samples prepared in this chapter were measured by the

thermal stimulation current test method introduced in Chapter 2. The thermal stimulation currents fitted by the summation of three relaxation processes expressed by the full current formula could be obtained in Matlab. The thermal stimulation current of each sample and its fitting values are shown in Fig. 3-12 (a) ~ (d). The black curve is the test data, and the red, blue and green curves are respectively the fitting current curves of the three relaxation processes. The pink curve is the fitting curve of the thermal stimulus current as the summation of the three fitting peaks. It can be seen that the fitting curve obtained by choosing different value of the parameters of the relaxation process using the method introduced in Chapter 2 fitted the original data well. The fitting parameters of the thermal stimulated current of the polyimide film samples prepared in this chapter are listed in Table 3-5.

Table 3-4 Parameters of Weibull Distribution of DC breakdown voltage of PI films with different mainchain structures

The sample name	PMDA - ODA	BPDA - ODA	BPDA - TRDA	BPDA - TMDA
Scale parameter /kV • mm <sup>-1</sup>	454.5	510.8	498.1	486.1
Shape parameter	10.10	13.55	15.60	11.23

It can be seen from Figure 3-12 that for these polyimide samples, the position of Peak3 is obviously lower than the respective glass transition temperature, and the value of  $E_a$  is basically above 1 eV, which is similar to the molecular chain movement in the literature. The activation energy of the heat engine is about 0.4eV, which proves that Peak3 is mainly related to the deep traps inside the material, but has little correlation with the movement of molecular chains. Although trap level of the Peak3 of PMDA-ODA is high, its trap density is small. The order of magnitude of  $N_{t3}$  is  $10^{13}$ , which is much smaller than that of three polyimide samples ( $N_{t3}$ ) synthesized by BPDA, of which the value is in the order of  $10^{14}$ . It indicates that more deep traps were generated inside the polyimide sample after the introduction of the biphenyl structure on the diamine, which may be related to the larger conjugated structure on the BPDA. The increase in the density of deep traps increases the probability of carriers being trapped, which limits the multiplication process of charge carriers in the medium and makes collision ionization less likely to occur thus the DC breakdown field strength is increased. This also confirms that the breakdown field strength of PMDA-ODA is less than the three polyimide samples synthesized by BPDA. The trap density of the three polyimide samples synthesized by BPDA is not much different, which shows that the introduction of ether bond and the change of benzene ring substitution position do not change the density of the deep trap. The  $N_{t3}$  of BPDA-TMDA is slightly smaller than that of BPDA-ODA because the introduction of ether bond reduces the effective density of the large conjugated system.

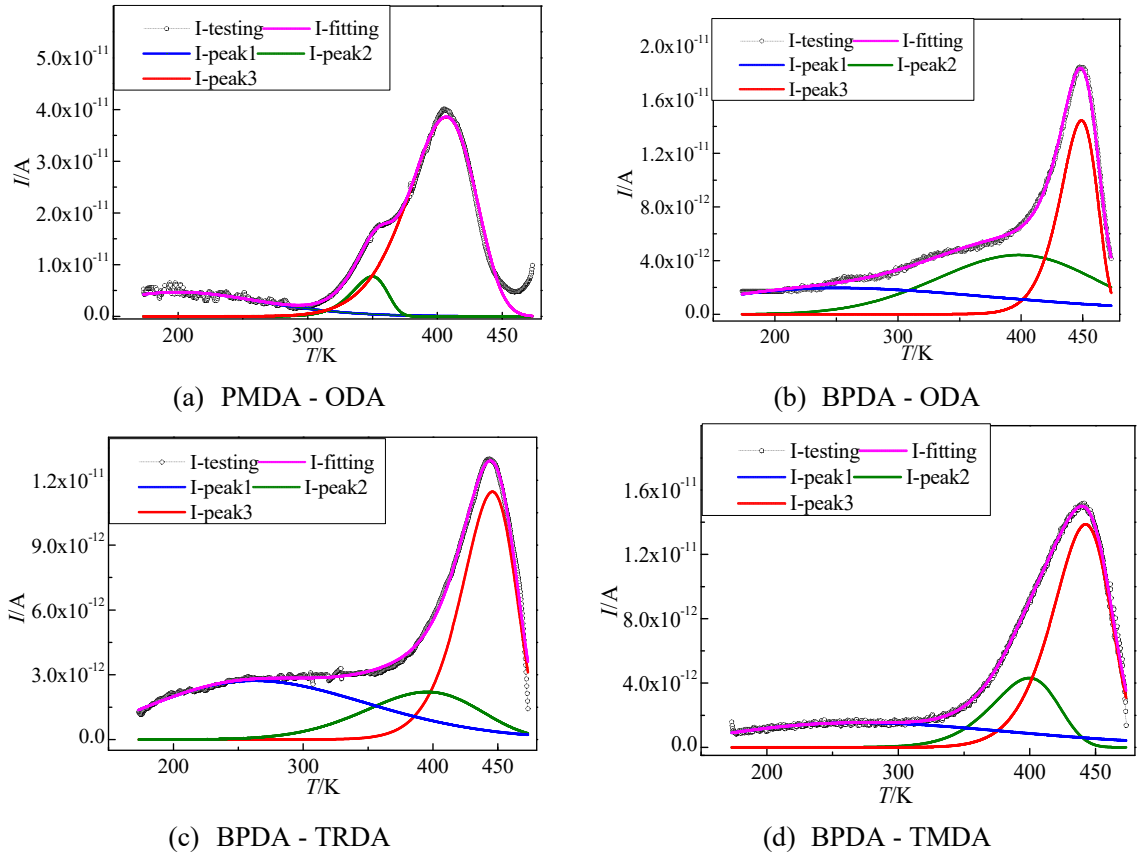

 Fig. 3-12 Comparison of thermal stimulation currents of PI films with different main chain structures<sup>3</sup>

Table 3-5 Fitting parameters of polyimide samples with different main chain structures

The fitting parameters		PMDA - ODA	BPDA - ODA	BPDA - TRDA	BPDA - TMDA
Peak1	$T/K_{peak1}$	$2.64 \times 10^2$	$2.86 \times 10^2$	$2.70 \times 10^2$	$2.66 \times 10^2$
	$E/eV_{a1}$	$6.75 \times 10^{-3}$	$5.16 \times 10^{-2}$	$3.95 \times 10^{-2}$	$5.09 \times 10^{-2}$
	$B/a. m_1^{-2}$	$1.77 \times 10^{-7}$	$1.58 \times 10^{-7}$	$1.12 \times 10^{-7}$	$1.63 \times 10^{-7}$
	$N/m_{i1}^{-3}$	$9.30 \times 10^{13}$	$4.21 \times 10^{14}$	$2.28 \times 10^{14}$	$4.12 \times 10^{14}$
	$\tau/s_{01}$	$1.99 \times 10^4$	$5.01 \times 10^2$	$8.78 \times 10^2$	$3.92 \times 10^2$
Peak2	$T/K_{peak2}$	$4.18 \times 10^2$	$4.04 \times 10^2$	$4.00 \times 10^2$	$4.00 \times 10^2$
	$E/eV_{a2}$	$5.87 \times 10^{-1}$	$2.18 \times 10^{-1}$	$5.17 \times 10^{-1}$	$2.94 \times 10^{-1}$
	$B/a. m_2^{-2}$	$4.46 \times 10^{-8}$	$1.84 \times 10^{-7}$	$8.43 \times 10^{-8}$	$7.07 \times 10^{-8}$
	$N/m_{i2}^{-3}$	$7.90 \times 10^{13}$	$4.80 \times 10^{14}$	$1.87 \times 10^{14}$	$1.80 \times 10^{14}$
	$\tau/s_{02}$	$6.55 \times 10^{-5}$	3.72	$2.41 \times 10^{-4}$	$2.78 \times 10^{-1}$
Peak3	$T/K_{peak3}$	$4.38 \times 10^2$	$4.49 \times 10^2$	$4.42 \times 10^2$	$4.46 \times 10^2$
	$E/eV_{a3}$	1.33	1.14	0.94	1.01
	$B/a. m_3^{-2}$	$3.84 \times 10^{-8}$	$1.72 \times 10^{-7}$	$2.37 \times 10^{-7}$	$1.80 \times 10^{-7}$
	$N/m_{i3}^{-3}$	$6.77 \times 10^{13}$	$4.79 \times 10^{14}$	$4.45 \times 10^{14}$	$4.51 \times 10^{14}$
	$\tau/s_{03}$	$1.92 \times 10^{-13}$	$8.02 \times 10^{-11}$	$2.38 \times 10^{-6}$	$3.99 \times 10^{-7}$

By combining the relative dielectric constant and breakdown strength of each thin film sample obtained in sections Chapter 3.3 and Chapter 3.4, formula (1-4) can be used to calculate the energy storage density of each polyimide thin film sample. Table 3-5 compares the energy storage density data of polyimide film samples with different mainchain structures. Fig. 3-13 is the comparison diagram of energy storage density, relative dielectric constant and breakdown strength of each thin film sample.

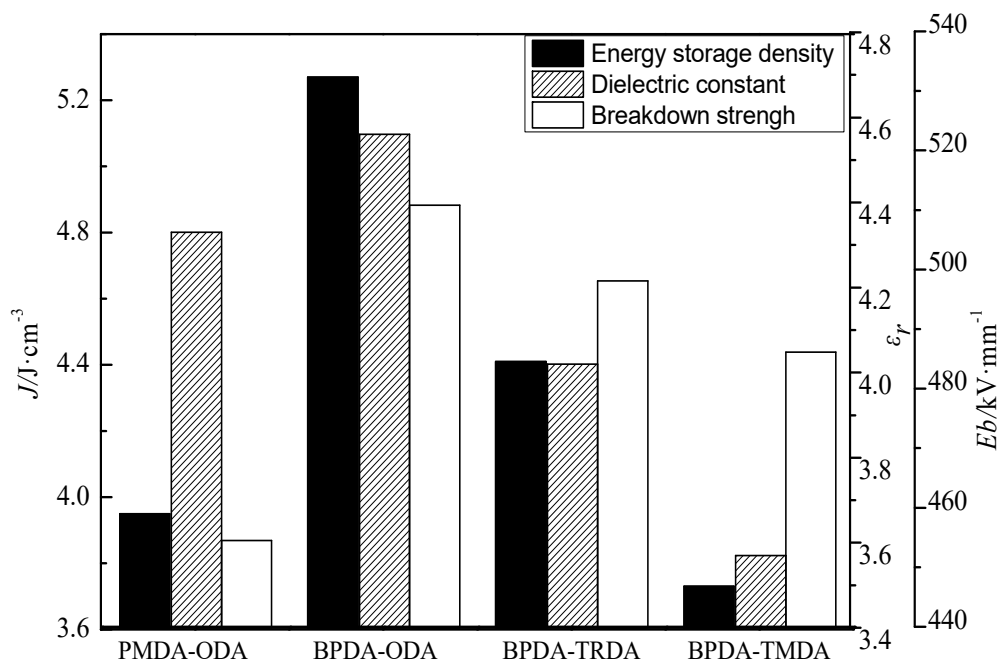


Fig. 3-13 Comparison of energy storage density of polyimide films with different mainchain structures

It can be seen that the effects of different main chain structures on the breakdown strength and relative dielectric constant of polyimide film samples exist simultaneously. The energy storage density of polyimide film samples prepared in this section is between  $3.73 J/cm^3$  and  $5.27 J/cm^3$ , higher than that of other pure polymer energy storage materials, such as BOPP ( $3.98 J/cm^3$ ) and PVDF ( $1.78 J/cm^3$ ), with certain advantages, which also shows that polyimide has great application potential in the field of energy storage from the data. When biphenyl structure is introduced into the dihydride, the existence of larger conjugated system is conducive to the formation of charge transfer complex, and the molecular chain is closely packed and strengthened, so that the breakdown strength and relative dielectric constant of polyimide are increased and the energy storage density is improved. Compared with the structure of PMDA-ODA, the breakdown strength of sample BPDA-ODA increased by 11%, and the corresponding energy storage density reached  $5.27 J/cm^3$ , which increased by 33.4%. When the ether bond (BPDA-TRDA) is introduced into the diamine or the substitution mode of amino group on the benzene ring is changed (BPDA-TMDA), the relative dielectric constant and breakdown strength will decrease, and the energy storage density will decrease by 16.3% and 15.4% respectively.

In order to increase the energy storage density of polyimide materials, large rigid conjugated structure is introduced into the dihydride, and the substitution mode of benzene

ring on the molecular main chain should be kept as the counterposition substitution mode with small spatial steric effect. Although the introduction of ether bond into the diamine main chain can improve the film-forming property of the material, it can reduce the energy storage density of polyimide film material.

Table 3-5 Comparison of energy storage densities of polyimide films with different mainchain structures

The sample name	PMDA - ODA	BPDA - ODA	BPDA - TRDA	BPDA - TMDA
Breakdown field strength /kV • mm <sup>-1</sup>	454.5	510.8	498.1	486.1
Relative dielectric constant	4.33	4.56	4.02	3.57
Energy storage density /J • cm <sup>-3</sup>	3.95	5.27	4.41	3.73

In this chapter, three diamines (ODA, TRDA, TMDA) and two dianhydrides (PMDA, BPDA) were selected to synthesize polyimide films with four different structures: PMDA-ODA, BPDA-ODA, BPDA-TRDA and BPDA-TMDA. FT-IR test, Differential Calorimetry Analysis, Thermogravimetric Analysis, broadband dielectric spectroscopy test, breakdown strength test, and thermal stimulation current test were conducted for each sample, and the results were compared and analyzed to draw the following conclusions:

(1) Adding a biphenyl or ether bond to the polyimide backbone or changing the substitution position of the amino group on the diamine on the benzene ring will not degrade the thermal performance of aromatic polyimides.

(2) Compared with PMDA-ODA, the energy storage density of BPDA-ODA increased by 33.4%. When the rigid biphenyl structure is introduced into the dihydride monomer, the biphenyl (rigid conjugated structure) and the carbonyl group in the imide ring form a larger conjugate system, which increases the breakdown strength of the polyimide film by 12.4%, thus increasing the energy storage density.

(3) Compared with BPDA-ODA, the breakdown strength of BPDA-TRDA also reduced by 11.9 kV/mm and the dielectric constant decreased 0.54, thus reducing the energy storage density by 16.3%. When ether bond is introduced into diamine monomer, the flexibility of molecular chain increases and the free volume increases but the dielectric constant decreases, while the increase of electron free path reduces the breakdown strength, which is not conducive to the increase of energy storage density.

(4) Compared with BPDA-TRDA, the breakdown strength and dielectric constant of BPDA-TMDA decreased, and the energy storage density decreased to 3.73 J/cm<sup>3</sup>, which is a decrease of 15.4%. When the substitution mode of amino in diamine on the benzene ring is changed from para substitution to interposition substitution, the steric hindrance effect is increased, the free volume and the degree of molecular chain distortion are increased, and the breakdown strength and dielectric constant are reduced, which is not conducive to the increase of energy storage density.



## 4 STUDY ON INFLUENCE ON ENERGY STORAGE CHARACTERISTICS OF INTRODUCING FLUOROMETHYL SIDE GROUPS INTO POLYIMIDE FILM

In order to compare the influence of different main chain structure of polyimide on energy storage characteristics, in this chapter two different diamine monomers, which are 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and 4,4'-(1,3-Phenylenedioxy)dianiline, and two different dianhydride monomers, which are 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride and 3,3',4,4'-Biphenyltetracarboxylic dianhydride, are selected to synthesize the four different polyimide film with different main chain structure according to the method and process mentioned in the second chapter and all of the samples are pretreated. This chapter mainly introduces the four polyimide film samples with different main chain structure, their structure characterization and their performance test results. The result of the tests are compared and the influence on the thermal properties, breakdown voltage and dielectric properties of polyimide film are analyzed when pendant group containing fluorine introduced in different part of monomers.

The introduction of fluorine atoms or fluorine-containing groups into the molecular structure of polyimides is an important method to modify the structure of polyimides. Due to the strong electronegativity of fluorine atoms, the conjugation of electron clouds in aromatic polyimides can be influenced, thus affecting the optical and electrical properties of polyimides. At the same time, fluorine-containing groups usually have a large volume, which can increase the distance between polyimide molecular chains and reduce the intermolecular forces, thus changing the thermal and dielectric properties of polyimide. Existing research often focused on the optical properties of fluorinated polyimide materials, dissolving properties, thermal properties. Some studies involving dielectric constants are mainly based on reducing dielectric constants as interlayer insulation of electronic devices. Mainly, there are not many studies on the effect of structural changes on energy storage characteristics, and there is a lack of comprehensive research on the effect of structural changes on energy storage characteristics from the side of dielectric constant and breakdown strength. From the previous research, the difference between the fluorinated side groups on the dianhydride and the diamine has a different effect on the thermal performance of polyimide optics. Starting from this idea, four polyimide film samples with similar structures, of which the main structure difference is whether contains fluorine-containing groups in diamine or dianhydride part, were synthesized using diamine monomers and dianhydride monomers containing trifluoromethyl or not.

Fig. 4-1 (a)~(e) is the molecular structure of dianhydride and diamine monomer selected to synthetic polyimide sample in this section, they are two different diamine monomers, which are 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane and 4,4'-(1,3-

Phenylenedioxy)dianiline, and two different dianhydride monomers, which are 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride and 3,3',4,4'-Biphenyltetracarboxylic dianhydride. Fig. 4-2(a)~(d) is the molecular structure of polyimide samples synthesized by using the above four monomers, which are BPDA-TRDA, 6FDA-TRDA, BPDA-FBDA and 6FDA-FBDA, respectively. The names are composed of the names of dihydride and diamine of the synthetic samples connected by hyphen. For example, 6FDA-FBDA is synthesized from 4,4'-(hexafluoroisopropyl) diphthalic anhydride (6FDA) and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (FBDA). BPDA-FBDA is synthesized from 3,3',4,4'-biphenyltetracarboxylic anhydride (BPDA) and 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane (FBDA). 6FDA-TRDA is synthesized from 4,4'-(hexafluoroisopropyl) diphthalic anhydride (6FDA) and 4,4'-(hexafluoroisopropyl) diphthalic anhydride (TRDA). BPDA-TRDA is synthesized from 3,3',4,4'-biphenyltetracarboxylic anhydride (BPDA) and 4,4'-(hexafluoroisopropyl) diphthalic anhydride (TRDA). For convenience of expression and description, abbreviations are used to replace full names in the sample names in the following text.

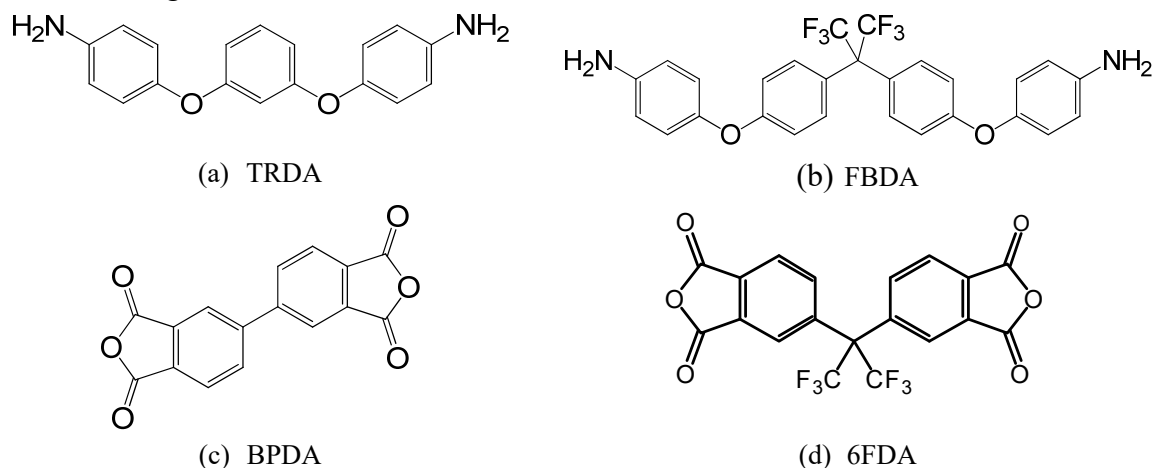


Fig. 4-1 Molecular structure of diamine and dianhydride monomer

Fig. 4-3 (a) ~ (d) is the spatial structure diagram of the four polyimide film samples with different main chain structures optimized by ChemBio3D Ultra software via MM2 according to the minimum energy principle. In the schematic ball model, the gray balls represent carbon atoms, the blue ones represent nitrogen atoms, the red ones represent oxygen atoms, the yellow ones represent fluorine atoms, and the pink ones represent isolated electron pairs. Comparing polyimides of four structures in Fig. 4-2 and Fig. 4-3, 6FDA-TRDA has two more fluoromethyl groups between the two benzene rings on the diamine compared with sample BPDA-TRDA. Meanwhile, the structure of biphenyl is destroyed and is no longer a rigid conjugate plane, and the rigidity of diamine chain segment is significantly reduced. Compared with sample BPDA-TRDA, sample BPDA-FBDA has two more fluoromethyl groups on the dianhydride. Due to the large volume of fluoromethyl groups and the strong electronegativity of fluorine atoms, the steric hindrance effect is large, and the molecular chain cannot stretch as well as BPDA-TRDA, the space structure is more distorted, and the conjugated structure on the dianhydride

is interrupted. In the sample 6FDA - FBDA, two fluoromethyl groups were introduced on the dihydride and diamine respectively, and the degree of twist of the chains was the highest. 1

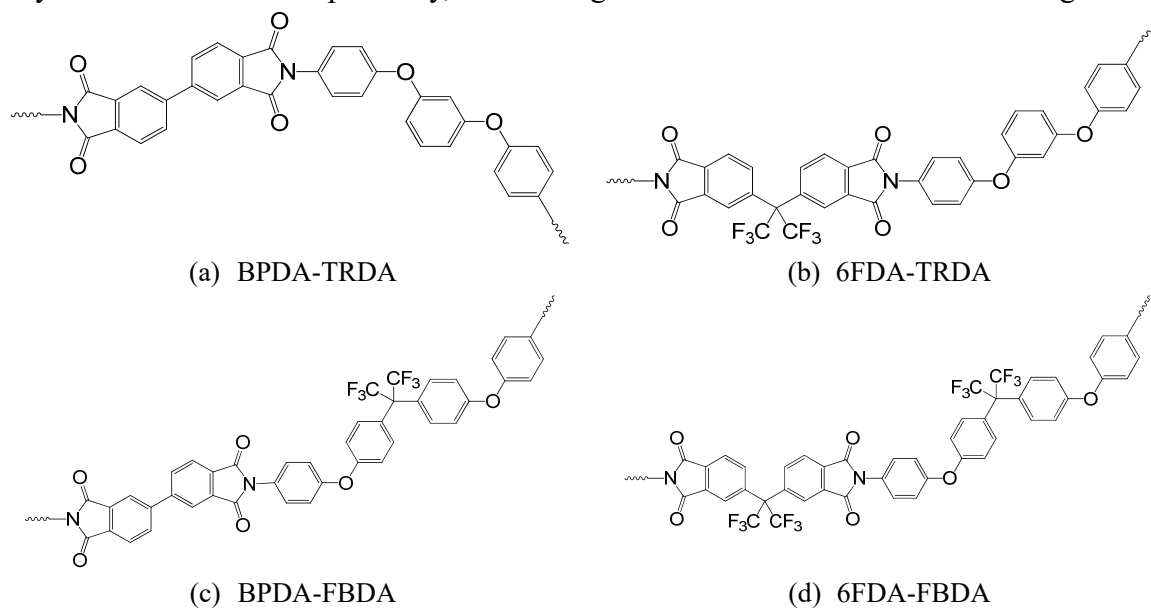


Fig. 4-2 Polyimides introducing fluoromethyl side groups

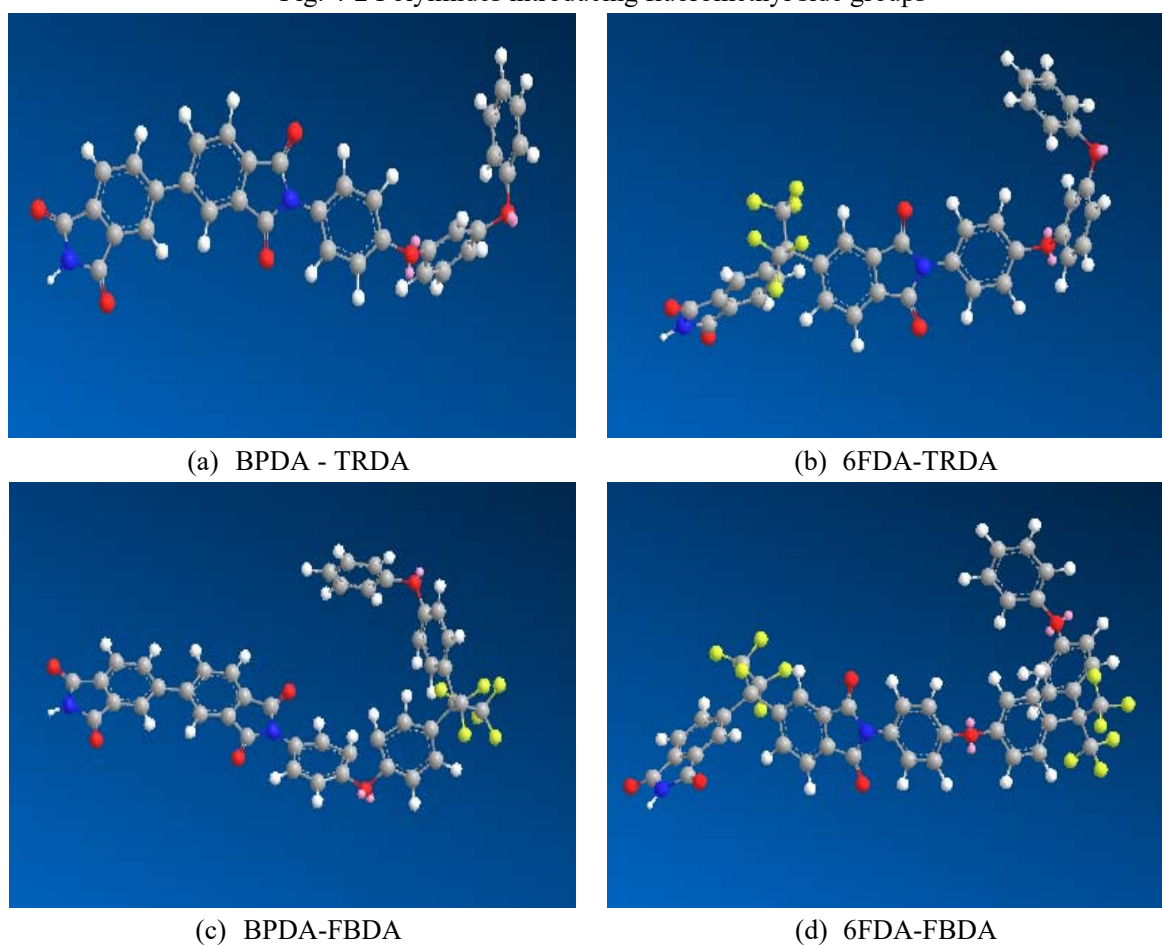


Fig. 4-3. Molecular spatial configuration of polyimides introducing fluoromethyl side groups

The structural characterization of the four polyimide film samples prepared in this section were achieved by FT-IR and the spectrum is shown in Fig.3-4. The *y*-axis is the percentage transmittance (%) and the *x*-axis is the wave number ( $\text{cm}^{-1}$ ). The characteristic spectral peak of each sample is shown in Table 4-1.

Taking the FT-IR spectrum of BPDA -FBDA as an example, the location and attribution of the bands of polyimide film samples were introduced as following. There is a =CH stretching vibration peak on the benzene ring between  $3000 \text{ cm}^{-1} \sim 3100 \text{ cm}^{-1}$ . Characteristic peaks of imide ring can be observed near  $1785 \text{ cm}^{-1}$  and  $1702 \text{ cm}^{-1}$  respectively. They represent symmetric (or in-phase) and asymmetric (or inverse-phase) stretching vibration peaks of carbonyl C=O on the pentamer ring, which are called imide band I and imide band II respectively. The C-N stretching vibration peak on the imide ring, also known as the imide band III, was observed near  $1366 \text{ cm}^{-1}$ . The peak at  $1094 \text{ cm}^{-1}$  and  $727 \text{ cm}^{-1}$  represents the deformation vibration of imide ring, which is the variable angle vibration of C=O, and the latter is also called imide band IV. The appearance of imide band I, band II, band III and band IV indicates that the product species contains imide rings. The three peaks observed near  $1587 \text{ cm}^{-1}$ ,  $1483 \text{ cm}^{-1}$ , and  $1446 \text{ cm}^{-1}$  are absorption peaks of typical benzene ring skeleton stretching vibration, and those near  $840 \text{ cm}^{-1}$  are absorption peaks of polysubstituted benzene ring bending vibration, indicating that the product contains polysubstituted benzene rings. Stretching vibration peak of aromatic interring ether bond -O- was observed near  $1239 \text{ cm}^{-1}$ , indicating the presence of aromatic ether in the sample. Stretching vibration peak of C-F bond can be seen near  $1203 \text{ cm}^{-1}$ , which indicates that C-F bond is included in the product. No typical vibration absorption peak of amino group was found within  $3200 \text{ cm}^{-1} \sim 3500 \text{ cm}^{-1}$ , indicating that there was no polyamide acid in the sample. In conclusion, the product is aromatic polyimide with ether bond and the polyamide acid is completely converted into polyimide in the process of thermal imidatio, which proves that the polyimide film with target structure is obtained. The analysis of BPDA-TRDA, 6FDA-TRDA and 6FDA-FBDA is similar to that of BPDA-FBDA. The infrared characteristic peaks of each sample are shown in Table 4-1.

Table 4-1 Infrared spectrometric analysis of polyimide introducing fluoromethyl side groups

The name of samples	Imide band I	Imide band II	Imide band III	Imide band IV	Aromatic ether	Polysubstituted benzene surface External bending vibration	Vibration of the bone of benzene ring	C - H vibration on benzene ring	Deformation and vibration of imide ring	The name of samples
BPDA - TRDA		1785	1709	1362	732	1219	845	1592, 1480, 1455		1094
6FDA - TRDA		1774	1703	1368	735	1230	840	1582, 1502, 1448	1189	1067
BPDA - FBDA		1785	1702	1366	727	1239	825	1587, 1483, 1446	1203	1094
6FDA - FBDA		1776	1705	1369	740	1236	828	1585, 1492, 1449	1202	1078

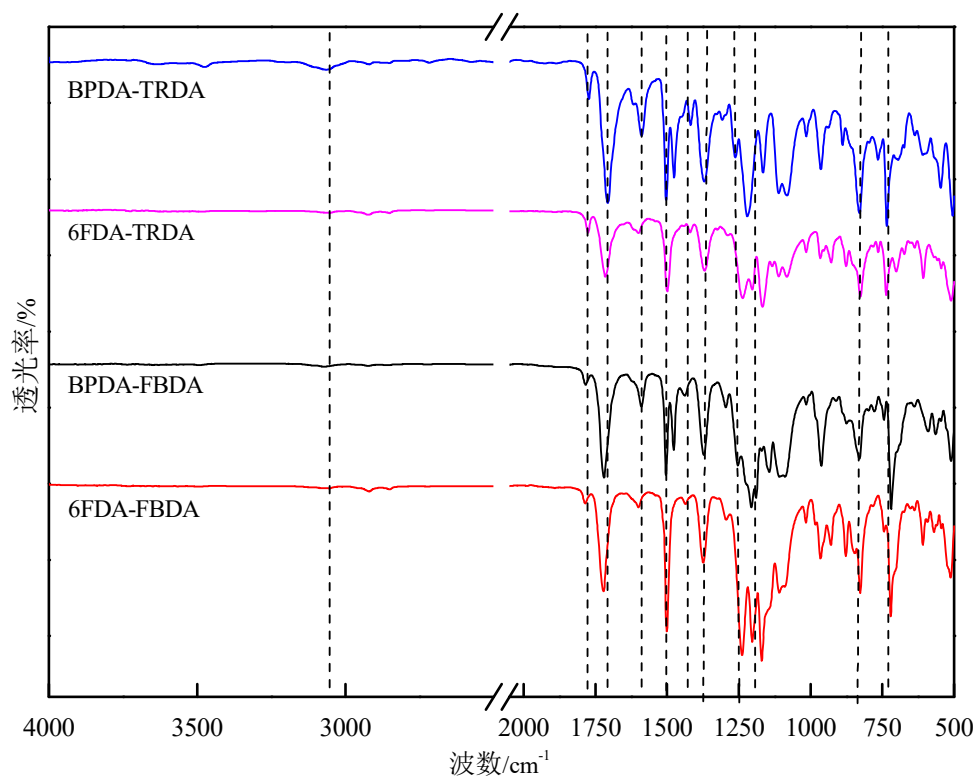


Fig. 4-4 FT-IR spectra of a polyimide introducing fluoromethyl side groups

Fig. 4-5 is the TGA curve of BPDA-TRDA, 6FDA-TRDA, BPDA-FBDA and 6FDA-FBDA prepared in this chapter, which is tested by thermo gravimetric analyzer in the nitrogen flow. The  $x$ -axis is the temperature, the range is 50-900 °C, and the  $y$ -axis is the weight percentage. The rising rate of temperature is 10°C/min. The thermal performance parameters of BPDA-TRDA, 6FDA-TRDA, BPDA-FBDA and 6FDA-FBDA is listed in Table 4-2. Where  $Td_{10}$  is the temperature at 10% weight loss,  $T_s$  is the initial decomposition temperature,  $T_d$  is the temperature where the maximum decomposition rate located. Char Yield is the percentage of sample residual weight at 900°C.

Table 4-2 Thermal properties of polyimide film introducing fluoromethyl side groups

The sample name	10% weight loss temperature $Td_{10}/^{\circ}\text{C}$	Initial decomposition temperature $T_s/^{\circ}\text{C}$	Maximum decomposition rate temperature $T_d/^{\circ}\text{C}$	Carbon residue rate / %	Glass transition temperature $T_g/^{\circ}\text{C}$
BPDA - TRDA	571.23	544.91	581.18	59.22	243.52
6FDA - TRDA	539.84	519.22	557.19	57.47	244.16
BPDA - FBDA	551.52	525.04	553.17	54.24	255.83
6FDA - FBDA	550.76	513.09	553.17	52.47	259.33

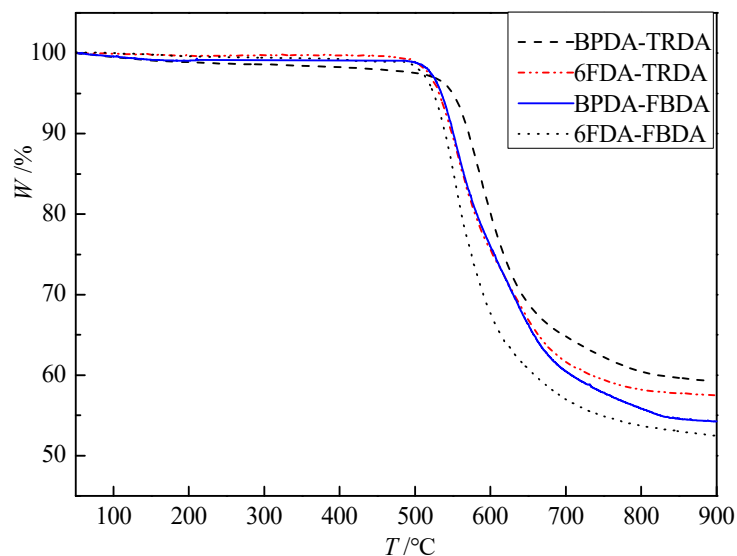


Fig. 4-5 TGA curves of polyimide film introducing fluoromethyl side groups

According to Fig.4-5 and Table 4-2, it can be found that the initial decomposition temperature range and 10% weight loss temperature range of the four polyimide film with different main chain structure are in 513°C~545°C and 540°C~571°C separately. The result shows that this kind of aromatic polyimide has excellent thermal stability, which is due to the existence of the rigid structure of benzene ring main chain that makes the molecular chain not easy to fracture under heating thus the thermal decomposition of materials are more difficult. Due to the high content of benzene rings in the molecular framework, the carbon residue rates of the four samples were all high, above 52.5% at 900 °C. The initial decomposition temperature  $T_s$  of 6FDA-TRDA was 519°C, which was lower than that of BPDA-TRDA, indicating that the thermal stability of polyimide was slightly decreased when trifluoromethyl was introduced into polyimide dihydride. Compared with 6FDA-TRDA and 6FDA-FBDA, the same conclusion was obtained, but the decline was smaller. Meanwhile, the initial decomposition temperature  $T_s$  of BPDA-FBDA was 525°C, which was lower than that of BPDA-TRDA, indicating that the thermal stability of polyimide was slightly reduced when trifluoromethyl was introduced into the diamine of polyimide. The same conclusion can be obtained by comparing 6FDA-TRDA and 6FDA-FBDA.

Introducing fluoromethyl groups into aromatic polyimide can make contribution to improve thermal stability, make the initial decomposition temperature of polyimide material decrease even to a certain extent, this is because the large volume of fluorine atoms with strong electronegativity of the fluoromethyl groups can make the conjugate system of the molecular chain cut or suppressed so that the rigidity of the molecular chain is reduced and the forming of charge transfer complex is obstructed. The relatively orderly arrangement of polyimide molecules are destroyed and the molecular chain of inter-atomic forces is reduced and so does the degree of close packing of molecular chain. So, the free volume of polyimide film increases and thermal stability of polyimide is reduced.

DSC curves of the four polyimide film samples was tested by Differential Scanning Calorimetry under nitrogen protection and the rising rate of temperature is  $10^{\circ}\text{C}/\text{min}$ . Fig. 4-6 shows the DSC curves of polyimide films with four different main chain structures. The  $x$ -axis is the temperature, the unit is  $^{\circ}\text{C}$ , the  $y$ -axis is the enthalpy change and the unit is  $\text{W}/\text{g}$ . The steps in the curve represent the glass transition process. As shown in Fig. 4-6, the Glass transition temperatures of the four polyimides were all above  $243^{\circ}\text{C}$ , indicating that the thermal properties of the four polyimides samples were all outstanding, and they had obvious advantages over other polymer materials when used at relatively high temperatures.

The  $T_g$  of BPDA-FBDA is  $256^{\circ}\text{C}$ , which is higher than that of BPDA-TRDA, indicating that when trifluoromethyl is introduced onto the diamine of polyimide, the glass transition temperature of polyimide increases. Comparing 6FDA-TRDA and 6FDA-FBDA, the same conclusion can be get. At the same time, the  $T_g$  of 6FDA-TRDA is  $243^{\circ}\text{C}$ , which is slightly higher than that of BPDA-TRDA, indicating that when trifluoromethyl is introduced into the dianhydride of polyimide, the  $T_g$  of polyimide has a slight increase. On the one hand, the strong electronegativity of trifluoromethyl group makes the trifluoromethyl groups on different molecular chains repel each other, which leads to an increase in the distance between molecules. The introduction of a molecular chain into the molecular chain increases the steric hindrance to a certain extent, the molecular chain has a higher degree of bending, and the molecular chain has a higher degree of entanglement, which hinders the rotation of the molecular chain. The effect of the latter is more strong and results in higher  $T_g$ . This is more pronounced when pendant trifluoromethyl groups introduce more flexible diamine segments.

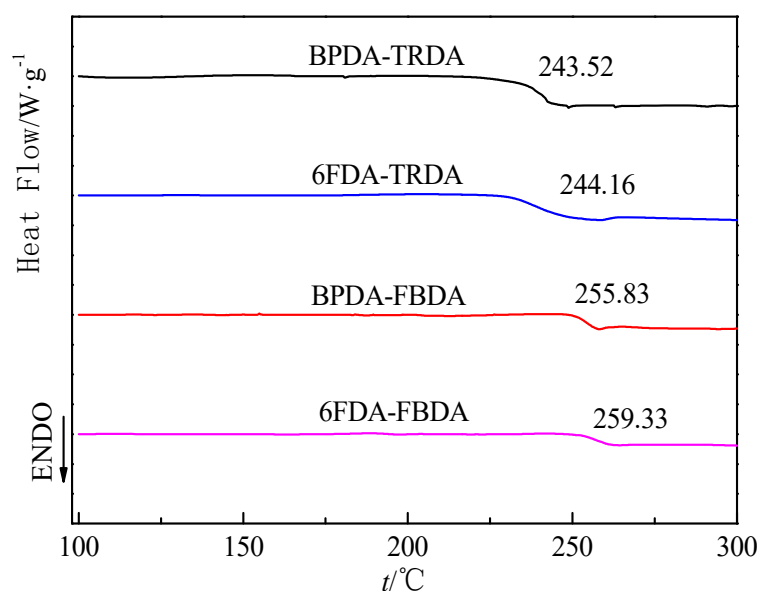


Fig. 4-6 DSC curve of polyimide film introducing fluoromethyl side groups

In this section, the Concept 80 broadband dielectric spectrometer is used to measure the broadband dielectric spectra of four polyimide film samples prepared with different main chain structures. The measurement temperature range is  $20^{\circ}\text{C}\sim 200^{\circ}\text{C}$ . The frequency is  $10^{-2}\text{ Hz}\sim 10^{-6}\text{ Hz}$ . The polarization process and dielectric loss of the polyimide film in the measurement

temperature range are studied through the analysis of the relative dielectric constant spectrum and the dielectric loss tangent spectrum, so as to further discuss the influence of different main chain structures on the dielectric properties of polyimide films.

Fig. 4-7 (a) ~ (d) shows the relative permittivity spectroscopy of BPDA-TRDA, 6FDA-TRDA, BPDA-FBDA and 6FDA-FBDA respectively. The ordinate is the relative permittivity, the x-axis coordinate is the logarithm of frequency. Table 4-3 shows the relative dielectric constant and tangent of dielectric loss Angle of polyimide film samples measured at 20°C and 50 Hz, as well as the electric saving dipole moments of each chain calculated after MM2 optimization in ChemBio3D Ultra. It can be seen that for the four samples, the relative permittivity basically decreases slightly with the increase of frequency, except that steps appear at high temperature (higher than 160°C) and low frequency. Taking BPDA-TRDA as an example, the relative dielectric constant at 20°C ranges from 3.75-4.14 with a small change in the frequency range of  $10^{-2}$  Hz ~  $10^6$  Hz, indicating that the prepared polyimide film sample has a high dielectric stability, with little change with frequency and temperature, and the dielectric constant at low frequency improves the temperature stability more after the introduction of fluorine-containing side group. From the discussion of Formula (3-1) Frohlich model in Chapter 3, it can be known the dielectric constant of the material can be increased by increasing the packing density of the molecular chain, decreasing the free volume to increase the electric dipole density  $N$  or increase the electric dipole moment  $u$ .

The relative dielectric constant of sample BPDA-FBDA decreased compared with BPDA-TRDA, indicating that the relative dielectric constant of polyimide decreased when trifluoromethyl was introduced into diamine part of polyimide. On the one hand, it can be seen from the Table 4-3 when the trifluoromethyl groups in introduced into polyimide, the electric dipole moment of the polymer linkage increased a lot due to the existence of fluorine atoms. But on the other hand, when bulk trifluoromethyl groups is introduced into diamine part, the distance between the molecular chain and chain will increase and the close packing of the molecular chain will decrease, so that the increase of free volume of the polymer and the reduction of the density of electric dipole relative dielectric constant are the important reasons. Fluorine atoms strong Electronegativity can suppressed the formation of charge transfer complex (CTC). Close packing of polyimide was formed originally by the CTC and it can be reduced and the order of molecular chain is reduced, makes the ability of electric dipole inside the material to orientate under external electric field decrease thus the relative dielectric constant is reduced. The same conclusion can be obtained by comparing 6FDA-TRDA and 6FDA-FBDA. At the same time, the relative dielectric constant of 6FDA-TRDA is slightly lower than that of BPDA-TRDA, but it is improved compared to 6FDA-FBDA. This is because the fluorine atoms in 6FDA-FBDA are limited to increase the free volume of the molecular chain, and the increase in the number of trifluoromethyl groups Its contribution to the electric dipole moment is greater. From the information of 6FDA-FBDA in Table 4-3, it can be seen that the calculated link electric dipole moment after each optimization by MM2 method is greatly improved.



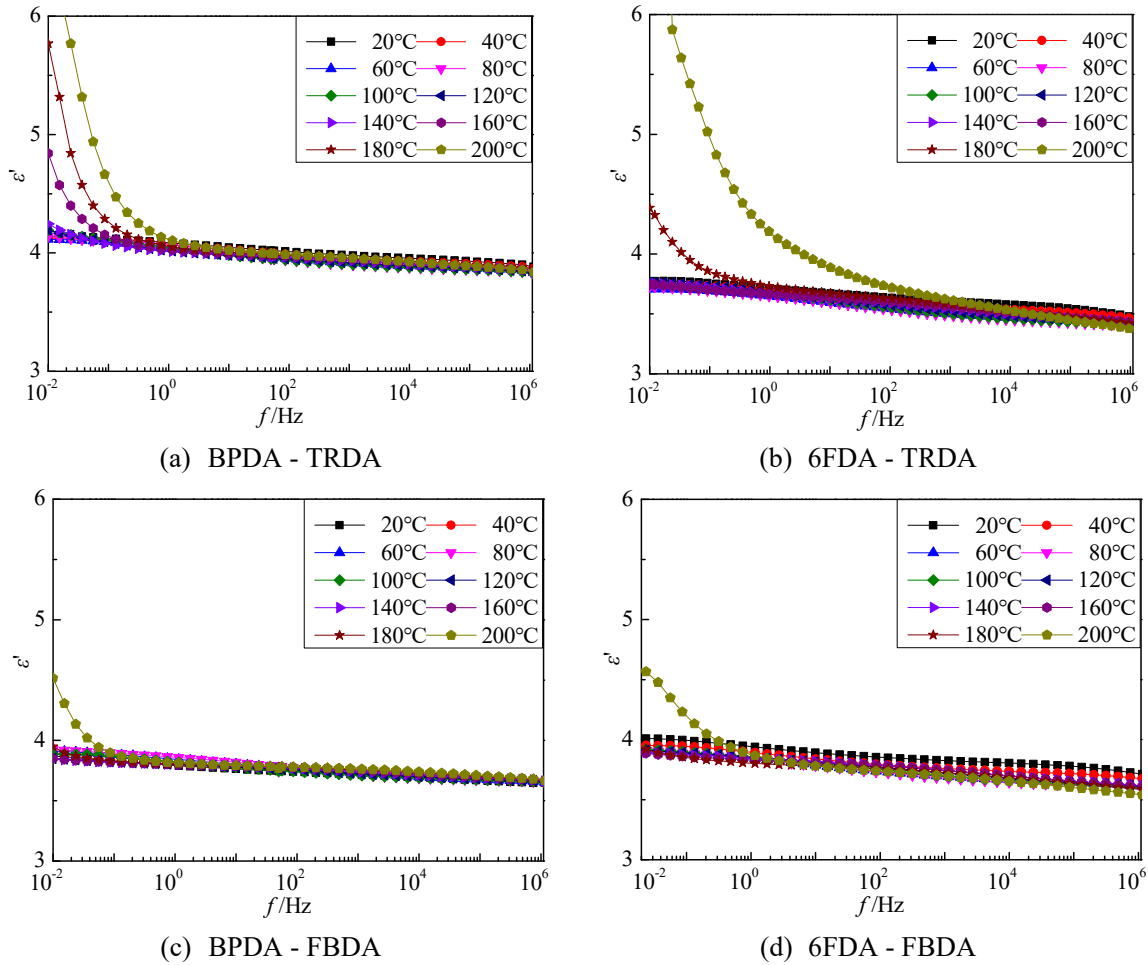


Fig. 4-7 Dielectric constant spectroscopy of polyimide film introducing fluoromethyl side groups

Table 4-3 The relative dielectric constant and the loss of the polyimide film introducing fluoromethyl side groups

The sample name	BPDA - TRDA	6FDA-TRDA	BPDA-FBDA	6FDA-FBDA
Chain saving dipole moment (Debye)	3.107	10.562	9.897	23.31
Relative dielectric constant (50Hz) <sub>r</sub>	4.02	3.86	3.74	3.81
Tangent of the dielectric loss Angle ( $\times 10^{-3}$ )	6.2	6.77	4.33	24.96

Fig. 4-8 (a) ~ (d) shows the loss spectroscopy of BPDA-TRDA, 6FDA-TRDA, BPDA-FBDA and 6FDA-FBDA respectively. According to Table 4-3, the dielectric loss of the four polyimide films are all smaller than the order of  $10^{-3}$ , indicating that polyimide materials have the advantages of small energy loss and high energy conversion rate as energy storage materials.

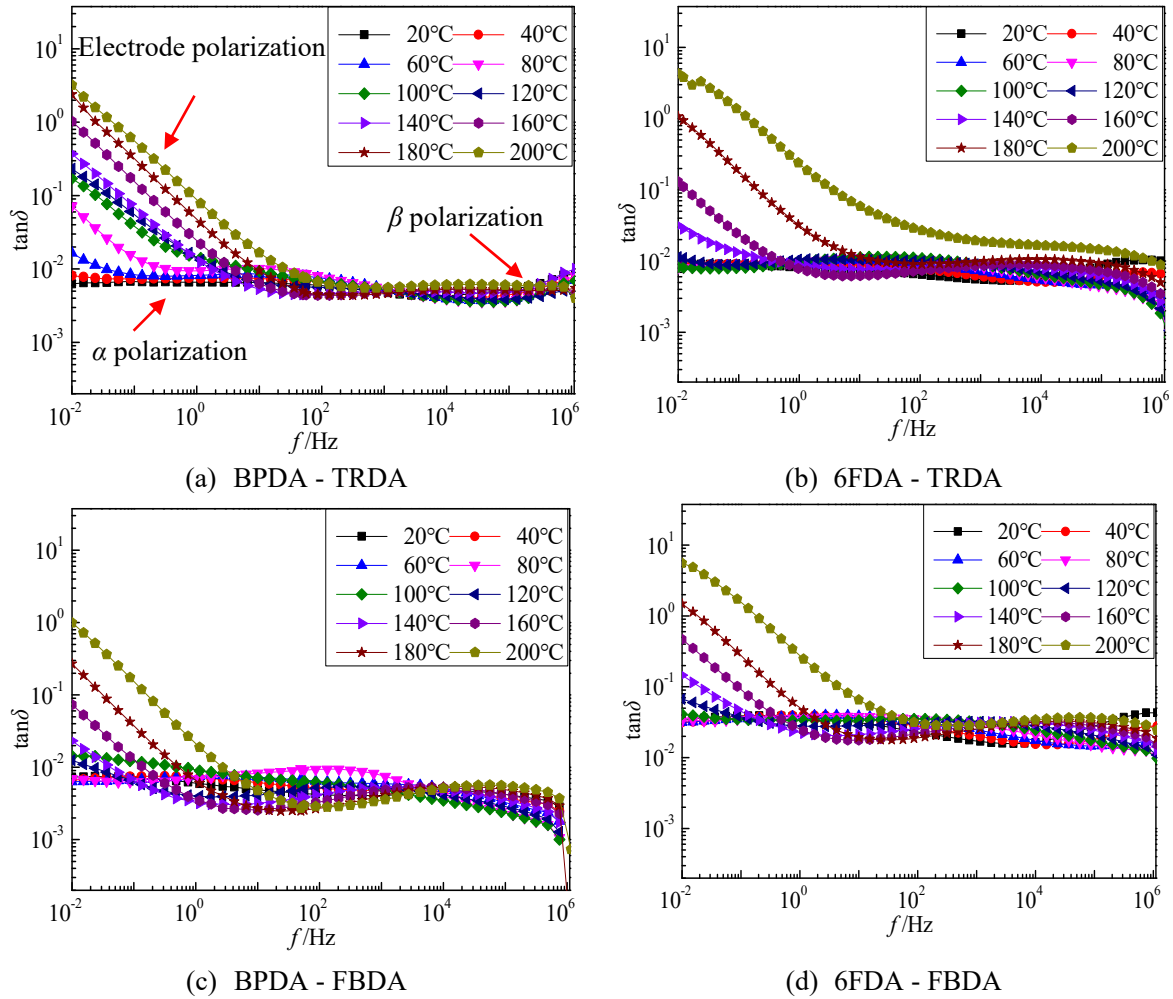


Fig. 4-8 Dielectric loss spectroscopy of polyimide film introducing fluoromethyl side groups

Taking BPDA-FBDA as an example to introduce the loss spectroscopy of PI films. It can be seen that there are three polarization processes in PI films in Fig. 3-9(a). Among them, the conductivity loss caused by electrode polarization is shown at high temperature and low frequency. This can be proved by that the slope of the imaginary part of the complex dielectric constant at the corresponding frequency at the log-log coordinate is -1 in Fig. 3-8.<sup>[60]</sup> A second loss peak can be seen at frequencies slightly above the electrode polarization, which is caused by the motion of the molecular chains., because of the large polyimide molecular weight the main chain of the molecule movement ability is weak, the polarization process occurred in low frequency band (usually <math> < 10^4 </math> Hz), and when the temperature rises, the polarization peak moves toward high frequency, it is because the molecular thermal motion increases with the increase of temperature, is advantageous to the molecular chain orientation in the electric field, dielectric relaxation process faster. A third loss peak can be seen at low temperature and high frequency (><math> > 10^4 </math> Hz). This loss peak is attributed to the polarization process caused by the turning of the dipole group (C=O, C-O, and C-N groups). Fig. 3-10 (a) ~ (d) respectively shows the polarization process of polyimide film samples with four different main chain structures, BPDA-TRDA, 6FDA-TRDA, BPDA-FBDA and 6FDA-FBDA Its ordinate is linear

coordinate and focuses on the polarization process at low temperature and high frequency (below 100°C and above 10<sup>4</sup> Hz).

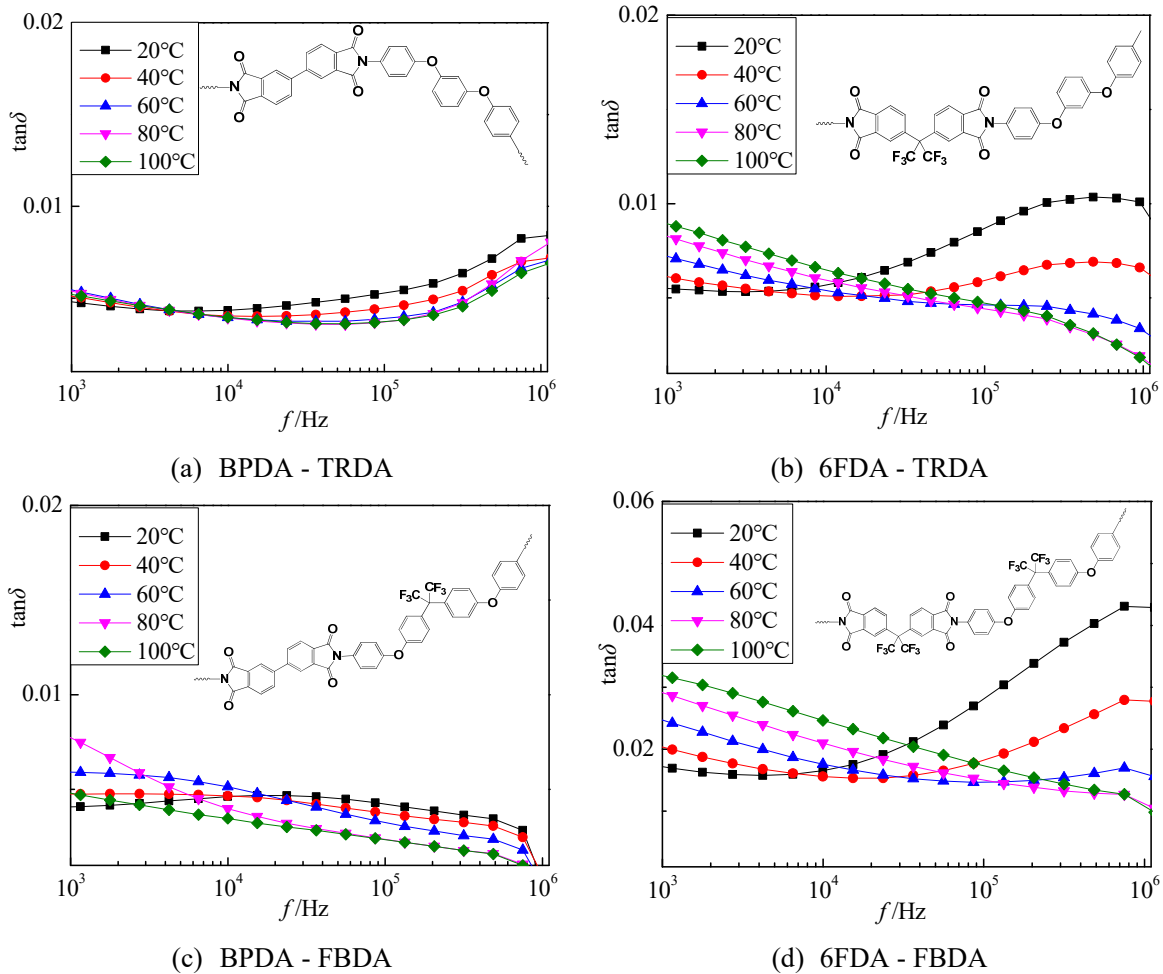


Fig. 4-9  $\beta$  polarization of polyimide introducing fluoromethyl side groups

Comparing Fig. 4-9(a) and 4-9(b)~(d), it can be found that the loss peaks of the depolarization process of samples BPDA-FBDA, 6FDA-TRDA, 6FDA-FBDA are higher than the peaks of BPDA-TRDA, the dielectric loss strength of the sample after the introduction of trifluoromethyl group on the dianhydride and diamine is greater. Because the large electronegativity of the fluorine atom makes it very strong in binding electrons after the introduction of a large volume trifluoromethyl group, which will reduce the conjugation of the original electrons and is suppress the formation of charge transfer complex (CTC). The degree of close packing formed by the CTC structure in the polyimide film sample is reduced and the distance between the molecular chains is increased, so the rotation and orientation of the molecular chains under the external electric field are more intense, so the loss caused by the  $\alpha$  polarization process is greater. When the trifluoromethyl group is introduced into the dianhydride, the above phenomenon will be more obvious because the original large conjugated structure formed by the biphenyl structure and the diamine is significantly reduced. In 6FDA-FBDA, the loss caused by the  $\alpha$  polarization process increased significantly. The loss intensity of the  $\alpha$  polarization at room temperature is higher than that of the other three samples

and reaches up to 0.024, which means that excessive introduction of trifluoromethyl will cause significant dielectric loss increase.

Comparing Figures 4-9(a) and 4-9(b)~(d), it can be seen that after the introduction of trifluoromethyl on the dianhydride, the  $\beta$ -polarization process of the sample is more obvious. The electric loss brought by  $\beta$ -polarization is greater because of the introduction of a new polar group trifluoromethyl which can be rotated. Compared with Figure 4-9(b) BPDA-FBDA and Fig. 4-9(a) BPDA-TRDA, it was found that after the introduction of trifluoromethyl on the diamine, the  $\beta$  polarization process of the sample is reduced, which may be related to the rigidity. The large volume of biphenyl structure restricts the rotation of trifluoromethyl. At the same time, due to the large volume of trifluoromethyl in BPDA-FBDA and the increase of the internal free volume of polyimide, which leads to the decrease of trifluoromethyl per unit volume. The number of dipole groups other than the group is reduced. From Fig. 4-9 (d) 6FDA-FBDA, it can be seen that when the trifluoromethyl structure is introduced into the dianhydride and diamine at the same time, the loss caused by the  $\beta$ -polarization process of the sample increases significantly compared to the BPDA-TRDA and the peak value of its loss peak rose from 0.008 to 0.042. Simultaneous introduction of trifluoromethyl into dianhydride and diamine will significantly deteriorate the dielectric loss of the synthesized polyimide.

In this paper, Origin software was used to achieve the two-parameter Weibull distribution failure probability graph of the breakdown strength of each sample, and the shape parameter and scale parameter were obtained. Blom method was used for scoring with a confidence interval of 95%. The shape parameter represents the dispersion of the data. The larger the shape parameter is, the smaller the dispersion of the sample data is. The scale parameter represents the breakdown strength of the measured material when the failure probability is 63.2% in weibull distribution. The unit is kV/mm, and it is used to represent the breakdown strength of the measured material. The breakdown voltage distribution diagram of the four samples is shown in Fig.4-10(a)~(d). The horizontal coordinate is the breakdown strength, and the unit is kV/mm. x-axis represents the probability of failure.

Table 4-4 shows the Weibull distribution parameters of the DC breakdown test of each polyimide film sample after processing data in Origin. It can be seen from the table that shape parameter of Weibull distribution of breakdown strength of each sample is above 10, indicating good dispersion of the experimental data. For the scale parameter, the breakdown strength of the four samples is generally higher than 483.4kV /mm, which indicates that the four polyimide samples obtained in this chapter have a high breakdown strength. The film sample BPDA-FBDA has the highest breakdown strength that reaches to 545.8kV /mm, which indicates very good breakdown performance. Compared with BPDA-TRDA, the breakdown strength of BPDA-FBDA increased from 498.1 kV/mm to 545.5 kV/mm. The results showed that the breakdown performance of polyimide was improved slightly when trifluoromethyl was introduced into the diamine of polyimide. The same conclusion can be obtained by comparing 6FDA-TRDA and 6FDA-FBDA. This is because fluorine atoms are highly electronegative and have a great ability to absorb electrons, so they can hinder the acceleration of free electrons under the external electric field and reduce the free path of electrons. The

increase of the free path of electrons reduces the probability of the electrons acquiring accelerated electrons in the amorphous region and increases the breakdown strength. However, the breakdown strength of 6FDA-TRDA was lower than that of BPDA-TRDA, indicating that the breakdown performance of polyimide was slightly reduced when trifluoromethyl was introduced into polyimide dihydride due to the cut off conjugated structure. The same conclusion can be obtained by comparing 6FDA-TRDA and 6FDA-FBDA. This is because although the introduction of trifluoromethyl itself is conducive to the improvement of the breakdown strength, in the process of the transformation of BPDA into 6FDA, the large conjugate system on the diamine is interrupted, and the presence of the large conjugate system makes it have less ability to generate high-speed electrons, which leads to the reduction of the breakdown strength. The effect of the latter is greater than that of the former, possibly because the volume of fluorine atoms is very small compared with the large conjugate system formed by biphenyl and imide bonds, and the probability of electron capture and obstruction is naturally greatly reduced. Therefore, when trifluoromethyl is introduced into diamine, the breakdown strength decreases.

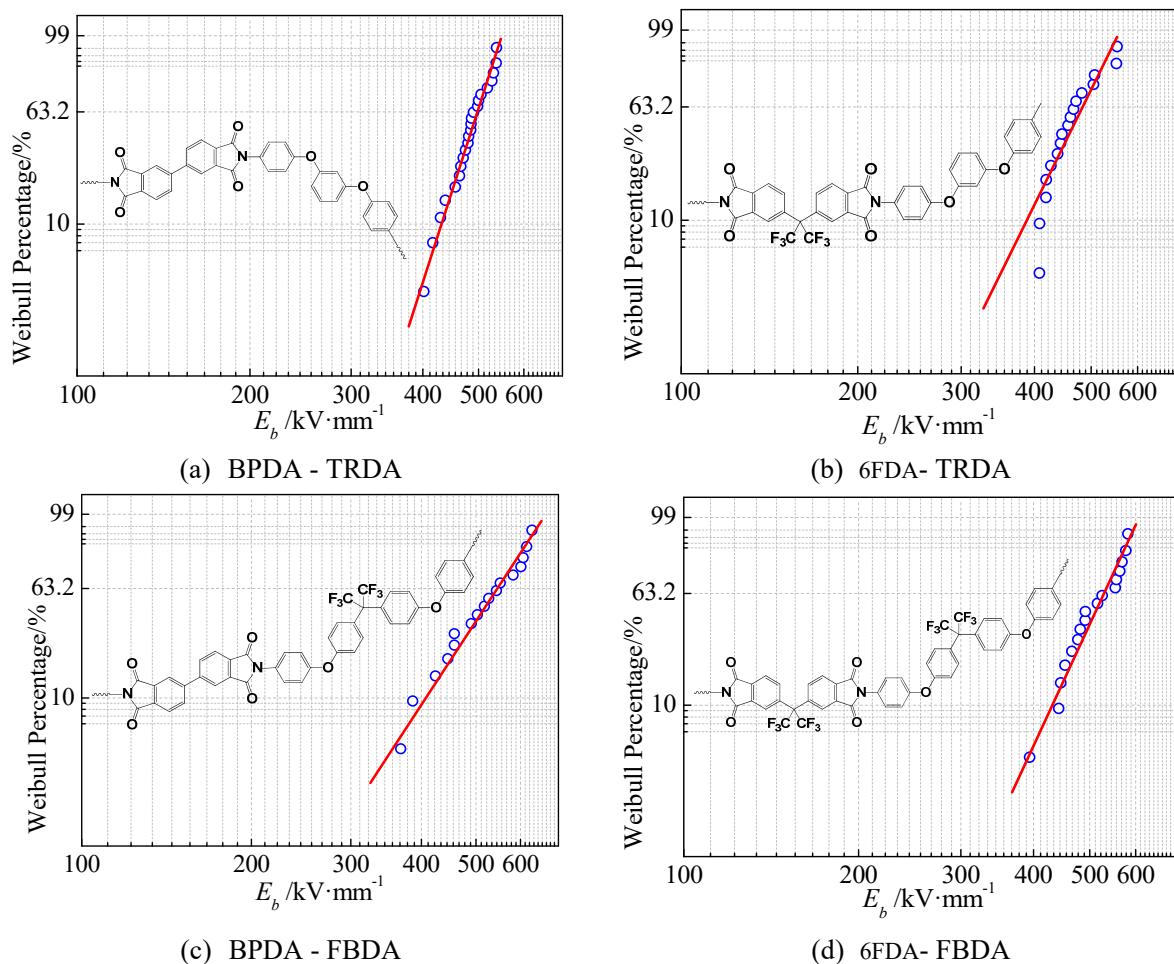


Fig. 4-10 Weibull distribution of breakdown strength of PI samples introducing fluoromethyl side groups

Table 4-4 Parameters of Weibull Distribution of DC breakdown voltage of PI films introducing fluoromethyl side groups

The sample name	BPDA - TRDA	6FDA - TRDA	BPDA - FBDA	6FDA-FBDA
Scale parameter /kV • mm <sup>-1</sup>	498.12	483.35	545.53	528.94
Shape parameter	10.10	15.60	13.55	11.23

Four different polyimide film samples prepared in this chapter were measured by the thermal stimulation current test method introduced in Chapter 2. The thermal stimulation currents fitted by the summation of three relaxation processes expressed by the full current formula could be obtained in Matlab. The thermal stimulation current of each sample and its fitting values are shown in Fig.4-11 (a) ~ (d). The black curve is the test data, and the red, blue and green curves are respectively the fitting current curves of the three relaxation processes. The pink curve is the fitting curve of the thermal stimulus current as the summation of the three fitting peaks. It can be seen that the fitting curve obtained by choosing different value of the parameters of the relaxation process using the method introduced in Chapter 2 fitted the original data well. The fitting parameters of the thermal stimulated current of the polyimide film samples prepared in this chapter are listed in Table 4-5.

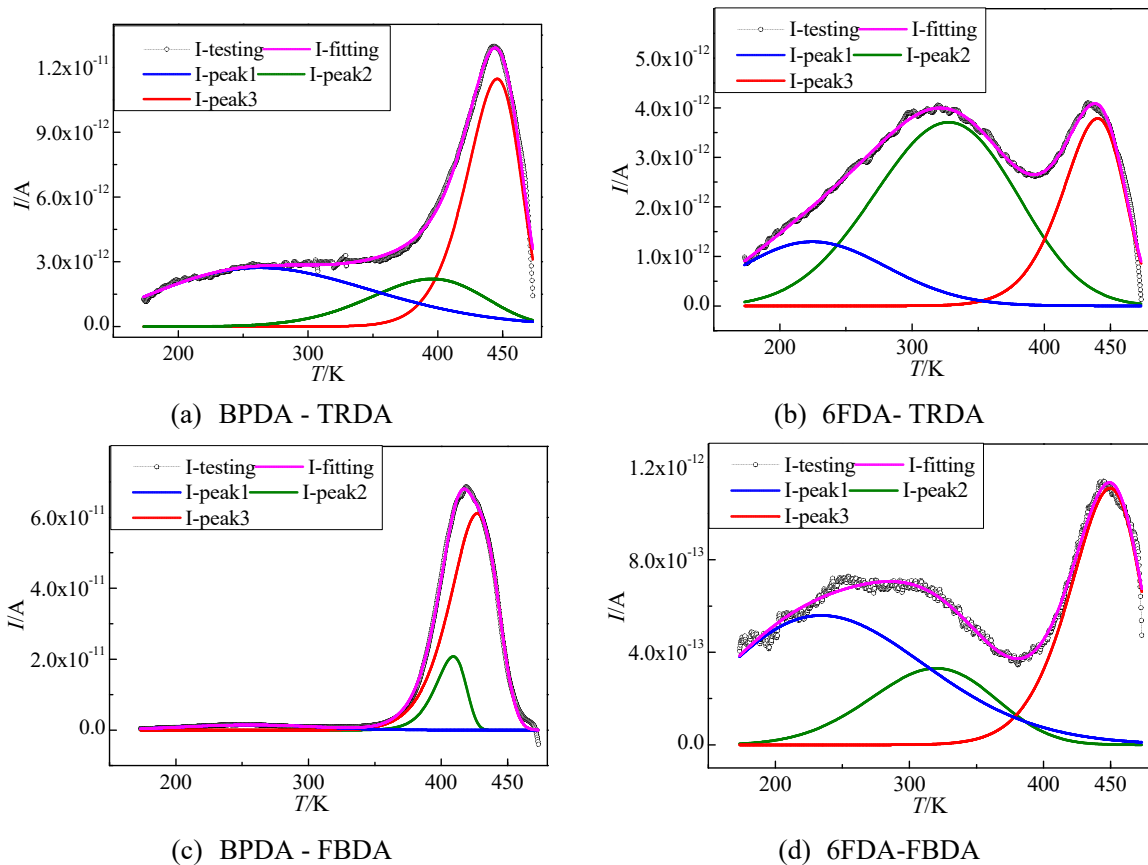


Fig. 4-11 Comparison of thermal stimulation currents of polyimide film introducing fluoromethyl side groups-

Table 4-5 Thermal stimulation current fitting parameters of polyimide samples introducing fluoromethyl side groups

The fitting parameters	BPDA - TRDA	6FDA - TRDA	BPDA - FBDA	6FDA - FBDA
$T/K_{peak1}$	266.12	256.55	214.13	233.72
$E/eV_{a1}$	0.05	0.09	0.06	0.05
Peak 1 $B/a. m_1^{-2}$	$1.63 \times 10^{-7}$	$5.35 \times 10^{-8}$	$3.20 \times 10^{-8}$	$2.60 \times 10^{-8}$
$N/m_{t1}^{-3}$	$4.12 \times 10^{14}$	$6.79 \times 10^{13}$	$6.15 \times 10^{13}$	$1.74 \times 10^{13}$
$Tau/s_{01}$	392.03	32.58	50.94	306.59
$T/K_{peak2}$	400.07	409.22	323.53	319.64
$E/eV_{a2}$	0.29	1.26	0.13	0.16
Peak2 $B/a. m_2^{-2}$	$7.07 \times 10^{-8}$	$1.86 \times 10^{-7}$	$1.64 \times 10^{-7}$	$1.18 \times 10^{-8}$
$N/m_{t2}^{-3}$	$1.80 \times 10^{14}$	$2.34 \times 10^{14}$	$3.15 \times 10^{14}$	$7.91 \times 10^{12}$
$Tau/s_{02}$	0.28	$1.02 \times 10^{-13}$	16.86	4.54
$T/K_{peak3}$	446.16	427.3	440.64	449.79
$E/eV_{a3}$	0.91	0.96	0.69	0.63
Peak3 $B/a. m_3^{-2}$	$1.80 \times 10^{-7}$	$8.52 \times 10^{-7}$	$6.72 \times 10^{-8}$	$2.25 \times 10^{-8}$
$N/m_{t3}^{-3}$	$4.51 \times 10^{14}$	$1.08 \times 10^{15}$	$1.25 \times 10^{14}$	$1.35 \times 10^{13}$
$Tau/s_{03}$	$3.99 \times 10^{-7}$	$3.98 \times 10^{-8}$	$8.32 \times 10^{-6}$	$6.47 \times 10^{-5}$

It can be seen from Figure 4-11 that for these polyimide samples, the position of Peak3 is obviously lower than the respective glass transition temperature, and the value of  $E_a$  is basically above 1 eV, which is similar to the molecular chain movement in the literature. While 6FDA-TRDA and 6FDA-FBDA, Peak3  $E_a$  dropped to 0.6. Combined with the discussion in the previous section, it was found that Peak3 mentioned above may be related to the large conjugated system composed of the carbonyl group of biphenyl and imide ring. Since the introduction of trifluoromethyl on the dianhydride cut off the large conjugated system consisting of biphenyl and carbonyl, the deep traps in 6FDA-TRDA and 6FDA-FBDA disappeared, and the activation energy and trap density at peak3 both decreased, so the introduction of pendant trifluoromethyl groups into the dianhydride is not conducive to the improvement of breakdown strength. It is worth noting that when the pendant trifluoromethyl group was introduced into the diamine part of the polyimide samples, the thermal stimulation current of the BPDA-FBDA sample found a peak with  $E_a$  of 1.26 eV at 409 K, and the trap density was  $2.34 \times 10^{14} \text{ m}^{-3}$ . Its appearance may be related to the synergistic effect of the conjugation structure of the fluorine atom and the dianhydride on hindering the acceleration

of free electrons under the external electric field. The increase of the deep trap density makes the breakdown strength of BPDA-FBDA increase because it enhances the carrier capture

probability, limits the carrier multiplication process in the medium and makes collision ionization difficult to occur.

By combining the dielectric constant and breakdown strength of each thin film sample obtained in sections 4.3 and 4.4, the energy storage density of each polyimide thin film sample can be calculated by using Formula (1-4). In Table 4-6 the energy storage density of polyimide film samples with fluorine side group compared with each other.

Table 4-6 Comparison of energy storage density of polyimide film introducing fluoromethyl side groups

The sample name	BPDA - TRDA	6FDA - TRDA	BPDA - FBDA	6FDA - FBDA
Breakdown field strength /kV • mm <sup>-1</sup>	498.1	483.3	545.5	528.9
Relative dielectric constant	4.02	3.86	3.74	3.81
Energy storage density /J • cm <sup>-3</sup>	4.41	3.96	4.93	4.71

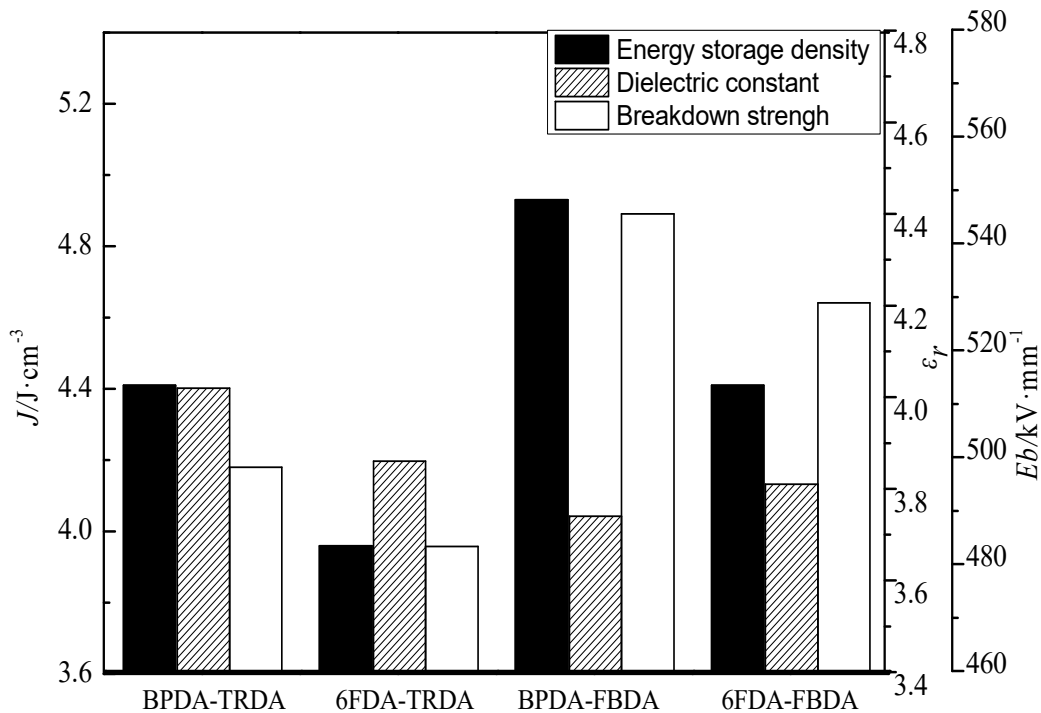


Fig. 4-12 Comparison of energy storage density of polyimide film introducing fluoromethyl side groups

As predicted, the dielectric constant of the sample decreased after the introduction of trifluoromethyl side groups into the polyimide molecules. By comparing three polyimides containing trifluoromethyl groups and BPDA-TRDA which is without trifluoromethyl groups, it can be seen that the dielectric constant decreases slightly after the introduction of trifluoromethyl groups (about 0.2). When trifluoromethyl is introduced into diamine part, the breakdown strength of the sample will increase. The energy storage density of the sample BPDA-FBDA reached 4.93 J/cm<sup>3</sup>, which was 12% higher than BPDA-TRDA, mainly because the breakdown strength was 9.5% higher than BPDA-TRDA. The energy storage density of



sample 6FDA-FBDA reached  $4.71 \text{ J/cm}^3$ , which was 18.9% higher than that of 6FDA-TRDA, mainly because its breakdown strength was 9.4% higher than that of 6FDA-TRDA. The energy storage density of 6FDA-TRDA was  $3.96 \text{ J/cm}^3$ , which was 10.2% lower than that of BPDA-TRDA. Similarly, the energy storage density of 6FDA-FBDA decreased by 4.5% compared with BPDA-FBDA.

The energy storage density of polyimide materials can be increased by introducing fluorine-containing side group on the diamine and increasing the breakdown strength of polyimide though the dielectric constant will slightly decrease. It should be avoided that the fluorine containing side group is introduced into the dihydride to destroy the original conjugated structure and degrade the energy storage performance.

In this chapter, two diamines (TRDA, FBDA) and two dianhydrides (6FDA, BPDA) were selected to synthesize polyimide films with four different structures: BPDA-TRDA, 6FDA-TRDA, BPDA-FBDA and 6FDA-FBDA. Infrared spectrum test, differential calorimetry test, thermogravimetric test, broadband dielectric spectroscopy, breakdown strength test, and thermal stimulation current test were performed on each sample, and the results were compared and analyzed, and the following conclusions were drawn:

(1) When introducing trifluoromethyl side groups into the anhydride or diamine monomer, due to the large volume of trifluoromethyl side groups, the space steric effect increases and the close packing of the molecular chain is influenced and the free volume increases at the same time, which make the thermal performance of polyimide slightly decrease but still maintain a high thermal stability and higher glass transition temperature.

(2) When trifluoromethyl group is introduced into the dihydride or diamine part, due to the increase of free volume, the number of electric dipole in unit volume decreases, the permittivity of polyimide film decreases slightly, and the permittivity of fluorine-containing samples decreases about 0.2 compared with BPDA-TRDA.

(3) When trifluoromethyl was introduced into diamine monomer, a deeper trap was introduced to increase the breakdown strength. compared with BPDA-TRDA, the breakdown strength of BPDA-FBDA was increased, and the energy storage density was increased by 12%, reaching  $4.93 \text{ J/cm}^3$ . Similarly, the energy storage density of 6FDA-FBDA reached  $4.71 \text{ J/cm}^3$ , which was 18.9% higher than that of 6FDA-TRDA. When trifluoromethyl was introduced into the dianhydride monomer, the original conjugated system of dianhydride was cut off and the breakdown strength was reduced. The energy storage density of 6FDA-TRDA was  $3.96 \text{ J/cm}^3$ , which was 10.2% lower than that of BPDA-TRDA. Similarly, the energy storage density of 6FDA-FBDA decreased by 4.5% compared with BPDA-FBDA.

## 5 Conclusions and Suggestions

In this paper, four diamine monomers (ODA, TRDA, TRDA, FBDA) and three dianhydride monomers (PMDA, BPDA, 6FDA) were selected to synthesize seven polyimide films with different structures: PMDA-ODA, BPDA-ODA, BPDA-TRDA, and BPDA-TRDA, 6FDA-FBDA. Infrared spectrum test, differential calorimetric analysis, thermogravimetric analysis, broadband dielectric spectroscopy, breakdown strength test and thermal stimulation current test were conducted on each sample to analyze its thermal performance, dielectric performance and breakdown performance, and then the energy storage density of each sample is evaluated, and the following conclusions were drawn:

(1) The thermal performance of aromatic polyimides is superior. The introduction of conjugated structure biphenyls in the main chain, the change of the substitution position of the amino group in the diamine on the benzene ring, the introduction of ether bonds or the introduction of trifluoromethyl side groups will not degrade the thermal performance of the aromatic polyimides.

(2) When the main chain structure of polyimide is changed with the goal of increasing the energy storage density, the free volume of the material should be reduced to improve the accumulation density of the molecular chain. As in the main chain of the dianhydride monomer adding rigid conjugate structure (PCB) is an effective way to improve the energy storage density of polyimide film, it to form large conjugated system together with carbonyl group of imide ring makes the deep trap increase in the number of polyimide film, thus improve the breakdown strength. At the same time, close packing of the molecular chain is improved so the dielectric constant is improved, which makes the energy storage density increases. However, when the flexible structure unit (ether bond) is introduced on the diamine monomer or the substitution of amino group on benzene ring of the diamine is changed from para substitution to meta substitution, the breakdown strength and dielectric constant of polyimide film will decrease due to the increase of free volume and the decrease of close packing density of the molecular chain, which is not conducive to the improvement of energy storage density.

(3) When fluorine-containing groups are introduced into aromatic polyimides, the dielectric constant of polyimide films decreases slightly due to the increase in free volume and the decrease in the number of electric dipoles per unit volume. The influence of the introduction of fluorine-containing groups on the breakdown strength of polyimide films is related to the location of the introduction: when trifluoromethyl is introduced into the dianhydride monomer, the original large conjugated system of dianhydride is destroyed, which will reduce the breakdown strength. When trifluoromethyl was introduced into diamine monomer, deep trap was introduced, which significantly increased the breakdown strength and thus was beneficial to increase the energy storage density of polyimide film.

(1) Only the aromatic dianhydride and aromatic diamine are selected to synthesis polyimide films in this thesis. Though the thermal performance is superior, the energy storage density remains to be further promoted. Considering the perspective of improving dielectric

constant, it may be a good way to introducing aliphatic side groups or other polar side groups such as nitrile into aromatic monomer to increase the polarity of the linkage to further enhance energy storage density for polyimide materials.

(2) From the perspective of improving the breakdown strength, on the premise of ensuring the film-forming property, the rigid conjugated structure larger than biphenyl can be introduced into dianhydride and trifluoromethyl can be introduced into diamine at the same time to further improve the energy storage density of polyimide materials.

(3) The change of molecular structure of monomer has a impact on the dielectric loss, breakdown strength and conductivity characteristics of polyimide samples under high temperature and the law and mechanism remain to be further explored.

## TO THANK

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## REFERENCE

- [1] Li Chunxi, Wang Jia, Ye Xuemin, et al. Development status and Prospect of New energy in China [J]. *Electric power science and engineering*, 2012, 28 (4) : 1-8.
- [2] Chu B, Zhou X, Ren K, et al. A dielectric polymer with high electric energy density and fast discharge speed [J]. *Science*, 2006:313
- [3] Li Hongzhong, FANG Yujiao, XIAO Baohui. Research on optimal Operation of regional integrated energy System considering generalized energy storage [J]. *Power Grid Technology*, 2019(9) : 3130-3138.
- [4] Armand M, Tarascon JM. Building better factories [J]. *Nature*, 2008, 451(7179):652-657.
- [5] Steele BC, Heinzl A. Materials for Fuel - Cell Technologies [J]. *Nature*, 2001, 414(6861):345-352.
- [6] Simon P, Gogotsi. Materials for electrochemical [M]// *Materials for Sustainable Energy: A Collection of peer-reviewed Research and Review Articles from Nature Publishing Group*. 2015.
- [7] Qin Chen, Yang Shen, Shihai Zhang, et al. Polymer based dielectrics with high energy storage density [J]. *Annual Review of Materials Research*, 2015, 45:433-458.
- [8] Rosa, Shen Jia-bin, GUO Shao-yun. Research progress of polymer-based dielectric composites with high energy storage density [J]. *Polymer Bulletin*, 2019, (08) : 14-21.
- [9] Barber P, Balasubramanian S, Anguchamy Y, et al. Polymer composite and nanocomposite dielectric materials for pulse power energy storage [J]. *Journal of electronic materials*, 2009, 2 (4) : 1697-1733.
- [10] Yuan Jinkai, Dang Zhimin. Research on high energy storage density all-organic composite thin film Dielectric materials [J]. *Insulation materials*, 2008, 41 (5) : 1-4.
- [11] *IEEE Transactions on Plasma Science*, 2002, 30(5):1939-1942.
- [12] Ho J, Jow TR, Boggs s. Historical introduction to technology [J]. *IEEE Electrical Insulation Magazine*, 2010, 26(1):20-25.
- [13] JK, Dang ZM, Yuan Yao SH, et al. The Flexible nanodielectric materials with high permittivity for power energy storage [J]. *Journal of Advanced materials*, 2013, 25 (44) : 6334-6365.
- [14] Li JY, Zhang L, Ducharme s. Electric energy density of dielectric nanocomposites [J]. *Journal of Applied Physics Letters*, 2007, living (13) : 132901.
- [15] Li Q, Han K, Gadinski MR, et al. Energy Storage: Capacitors from solution-processed ternary ferroelectric polymer nanocomposites [J]. *Advanced Materials*, 2014, 26(36):6356-6356.
- [16] Zhang X, Shen Y, Xu B, et al. The Giant energy density and improved discharge efficiency of solution - processed polymer nanocomposites for dielectric energy storage [J]. *Journal of Advanced Materials*, 2016, 28 (10) : 2055-2061.
- [17] Wei-dong sun. Preparation of polyimide matrix composites and their high temperature dielectric properties [D]. Beijing: Tsinghua University, 2017.
- [18] Li Zhanxiong, Wang Pacesetter, Ou Yuxiang. High-temperature polymer [M]. Beijing: Chemical Industry Press, 2007.
- [19] Tan D, Zhang L, Chen Q, et al. Polymer films of high-temperature Materials [J]. *Journal of Electronic Materials*, 2014, 43(12):4569-4575.
- [20] Fan Shu-shi, Liang Deqing, Yang Xiang-yang. Energy storage materials and Technology [M]. Beijing: Chemical Industry Press, 2004.
- [21] Bogert MT, Renshaw R. 4-amino -0-Phthalic Acid and Some of Its Derivatives [J]. *Jamchemsoc*, 1902, 30(7):1135-1144.

- [22] Edwards WM, Maxwell's RI... Polyimides of pyromellitic acid: U.S. Patent 2,710,853[P].1955-6-14.
- [23] Wangxiaolong. Synthesis and properties of novel main chain polyimides containing pyridine rings [D].Lanzhou: Lanzhou University, 2007.
- [24] Huang Xiaohua. Synthesis and Properties of novel functional polyimides [D].Shanghai: Shanghai Jiao Tong University, 2011.
- [25] He Tianbai, Hu Hanjie.Functional polymers and new Technologies [M].Beijing: Chemical Industry Press, 2001.
- [26] Ding.Polyimide.Chemistry, relationship between structure and properties and materials [M].Beijing: Science Press, 2006.
- [27] Xia Zuo Hun, Xia Lin.Application of polyimide insulation material in motor [J].Aging and application of synthetic materials, 2003,032 (002) : 35-38.
- [28] Jiang LY, Leu CM, Wei h. K Layered silicates/fluorinated polyimide nanocomposites for advanced dielectric materials applications [J]. Journal of advanced materials, 2002, 14 (6) : 426-429.
- [29] Yan Hongxia, Liang Guozheng, Ma Xiaoyan et al.Polyimide inorganic nanohybrid material [J].Polymer Bulletin, 2003(06) : 29-33+44.
- [30] Jia-ming wang.Application prospect and development suggestion of polyimide fiber [J].Acetaldehyde acetic acid chemical industry, 2012,29 (2) : 23-27.
- [31] Zhang Qinghua, Chen Dajun, DING Mengxian.Polyimide fibre [J].Polymer Bulletin, 2001, (5) : 68-74.
- [32] Xin.Advances in the application of polyimide foams in aerospace vehicles [J].Dual-use Technologies and Products, 2018, (22) : 64-68.
- [33] Wang Jin, LIU Tao, FENG Shudong.Current situation and research progress of polyimide adhesives [J].Chemical New Materials, 2006, (12) : 4-8.
- [34] Okamoto KI, Fuji M, Okamoto S, et al. Gas reaction properties of poly (ether imide), was mentioned in next year. Macromolecules,1995,28(20):6950-6956.
- [35] Al Masri M, Kricheldorf HR,Fritsch d. New polyimides for gas separation. 1. Polyimides derived from substituted terphenylenes and 4, 4 - (hexafluoroisopropylidene) diphthalic anhydride [J]. Journal of Macromolecules, 1999, 32 (23) : 7853-7858.
- [36] Watanabe Y, Shibasaki Y, Ando S,Et al. A new positive-type photosensitive -developable alicyclic Polyimide based on poly (Amic acid silylester) and Diazonaphthoquinone as A photosensitiveCompound [J]. Chemistry Of Materials, 2002, 14(4):1762-1766.
- [37] Kim KH, Jang S, Harris FW. Synthesis and characterization of photosensitive polyimides for optical applications[J]. Macromolecules,2001,34(26):8925-8933.
- [38] Yu Zhong, Wei Wei, Hou Xun.Fd-bpm Analysis of a compact fluorinated polyimide multimode interferometer WDM [J].Optics and Optoelectronics Technology, 2005, (3) : 2-5.
- [39] Wang F, Chen K, Sun W, et al. 32-channel arrayed waveguide multiplexer using low loss fluorinated operating around 1550 nm[J]. Optics Communications,2006,259(2):665-669.
- [40] Thelakkat M, Schmitz C, Neuber C, et al. Materials screening and combinatorial development of thin film multilayer electro - optical devices[J]. Macromolecular Rapid Communications,2004,25(1):204-223.
- [41] Kanno M, Kawakami H, Nagaoka S, et al. Biocompatibility of fluorinated polyimide[J]. Journal of Biomedical Materials Research,2002,60(1):53-60.
- [42] Chen Wei, ZHENG Hua, LIU Peipei, et al.Biocompatibility of polyimide film electrodes with rat optic glial cells [J].Journal of Neuroanatomy, 2009, (03) : 10-14.
- [43] Shi Lixin, Cui Lianfu.Studies on polyimide synthesis [J].Journal of Shenyang University of Chemical Technology, 1994, (04) : 272-276.

- 
- [44] Yang Shiyong, FAN Lin, Chen Jian-sheng, et al. Research progress of high-performance polyimide materials [C] // advanced Polymer Materials Symposium of Chinese Academy of Sciences and annual meeting of Engineering Plastics Committee of China Plastics Processing Industry Association, 2008.
- [45] Cotter RJ, Sauers CK, Whelan JM. The short of N - substituted isomaleimides [J]. *Journal of Organic Chemistry*, 1961, 26 (1) : 10-15.
- [46] Zheng Jianbang, Ma Rong, Cao Meng, etc. Optical and electrical properties of polyimide films prepared by vapor deposition [J]. *Semiconductor optoelectronics*, 2001, 22 (6) : 44-48.
- [47] Dickinson PR, Sung CSP. The Kinetics and mechanisms of thermal imidization studies by UV - visible and fluorescence spectroscopic techniques [J]. *Journal of Macromolecules*, 1992, 25 (14) : 3758-3768.
- [48] Pyun E, Mathisen RJ, Sung csp. Kinetics and mechanisms of thermal imidization of a polyamic acid by ultraviolet-visible spectroscopy [J]. *Macromolecules*, 1989, 22(3):1174-1183.
- [49] Bing-hai li. Synthesis of polyimides by nucleophilic substitution condensation of bis and Bis [J]. *Applied chemistry*, 1985, 2 (2) : 94.
- [50] Din-hart RA, Wright ww. A study of some properties of aromatic imides [J]. *Macromolecular Chemistry & Physics*, 1971, 143(1):189-206.
- [51] Treufeld I, Wang DH, Kurish BA, It is important that et al. Septuagary energy storage using polar polyimides with nitrile groups directly attached to the main chain [J]. *Journal of Materials Chemistry A*, 2014, 2(48):20683-20696.
- [52] Chen G, Lin J, Wang X, It is important that it is important that et al. Three-layer Structure Design for septuagens the Energy efficiency and breakdown strength of KTaNbO/polyimide nanocomposite films with high thermal stability [J]. *Journal of Materials Science: Septuagens*, 2001. *Materials in Electronics*, 2017, 28 (18) : 13861-13868. 0.50.53
- [53] Ai D, Li H, Zhou Y, et al. Tuning nanofillers in Situ prepared polyimide nanocomposites for high - temperature capacitive energy storage [J]. *Advanced energy Materials*, 2020, 10(16):881-888.
- [54] Li Hongyan, GUO Lei, Liu Bin, et al. Dielectric properties of polyimide/nano-titanium oxide composite films [J]. *Insulation materials*, 2005, 38 (6) : 30-33.
- [55] Stuart BBH. Fundamentals and applications [J]. *Experimental Thermodynamics*, 2004, 41(4):325 -- 385.
- [56] Ying, L. Xiaolong c. A novel method for the insulation of HV XLPE cable based on electrical treeing tests [J]. *IEEE Transactions on Dielectrics and electrical insulation*, 2014, 21(4):1540-1546.
- [57] Joarder A, Krishna H, Kundu d. Inferences on Weibull parameters with conventional type-i censoring [J]. *Computational Statistics & Data Analysis*, 2011, 55(1):1-11.
- [58] Maximum likelihood estimation in the Weibull distribution based on complete and on. *Technometrics*, 1965, 7(4):579-588.
- [59] Feng Y, Hasegawa Y, Suga T, et al. The Tuning conformational H - bonding arrays in aromatic/alicyclic polythiourea toward high energy - storable dielectric material [J]. *Journal of Macromolecules*, 2019, 52 (22) : 8781-8787.
- [60] Kremer, F Schonhals A, et al. *Broadband dielectric spectroscopy* [M]. Springer Science & Business Media, 2002.
- [61] Kao KC *Dielectric phenomena in solids* [M]. Elsevier, 2004 573-581.
- [62] Alagiriswamy AA, Narayan KS, Raju g. Relaxation processes in aromatic polyimide [J]. *Journal of Physics D: Applied Physics*, 2002, 35(21):2850.