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Overview of Polyimide Dielectrics

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1.1 Introduction

The advancements in aerospace and new energy technologies have accelerated the demand for high-temperature-resistant and high-performance polymer dielectric materials. Researchers have developed a range of specialty engineering plastics such as polyphenylene sulfide (PPS), polytetrafluoroethylene (PTFE), poly(ether ether ketone) (PEEK), polyethersulfone (PES), and polyimide (PI) [1]. PI is a class of polymer that contains an imide structure in the molecular backbone. The rigid imide ring gives PI excellent high-temperature resistance; thus, only cyclic polyimides are of practical application. PI was first reported in 1908, [2] and DuPont commercialized Kapton films in the mid-1960s. Since then, PI has entered an era of booming growth.

PI has been fully developed as a promising polymer, especially in the field of insulating and functional materials. The reason for the considerable interest in PI, compared to other high-temperature-resistant polymers, is due to its high structural designability, numerous synthesis and processing methods, as well as its outstanding comprehensive performance and wide range of applications.

This chapter provides a concise overview of the design, fabrication, and application of PIs. Firstly, the PI is introduced from a structural perspective in order to provide an overview of the general relationship between structure and function, which will then be used to guide the subsequent design. Then, the synthesis of PI and the preparation of different types of PI dielectric materials are discussed. Subsequently, the various properties of PI and the corresponding application areas are summarized. Finally, the key points of PI dielectrics are summed up and the future development is prospected.

1.2 Structure Design of Polyimide

The process of designing a polyimide usually involves careful planning of its molecular structure to ensure that the resulting material has the desired properties.

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PI consists of alternating electron donors (diamines) and electron acceptors (dianhydrides). Therefore, designing PI can be realized by changing the structure of diamine and dianhydride. More than 1000 diamines and more than 400 dianhydrides are currently used to synthesize PIs, resulting in thousands of PIs with different structures. Here, only some common structure–property relationships are briefly described, such as thermal, mechanical, and electrical properties.

For PI, during aromatic heterocyclic polymerization, the glass transition temperature (T_g) is mainly related to the relevant chain length of the macromolecule and the intermolecular forces. PI has a higher T_g and thermal stability than the corresponding polyether or polyester due to intermolecular forces other than van der Waals forces. Intramolecular or intermolecular charge transfer interactions are induced between the electron acceptor and electron donor of the PI, as shown in Figure 1.1. The charge transfer effect is related to the electron affinity of the dianhydride (or the hole affinity of the diamine) and the conformation of the molecular chain. It can be qualitatively argued that increasing the electron affinity of the dianhydride enhances interchain interactions, i.e., increases T_g . Intramolecular charge transfer is greatest when the electron donor and the electron acceptor are co-planar, but least when they are perpendicular. The planar structure between the electron donor and acceptor can be disrupted by making neighboring substitutions to the C—N bond. For example, with neighboring methyl substitution of diamines, the site-blocking effect disrupts the coplanar structure and increases the rigidity of the molecular chain, resulting in an improved T_g .

The mechanical properties of polymers are mainly influenced by the molecular structure, which determines the intramolecular chemical bonding forces and intermolecular forces. For example, increasing the polarity of the PI or creating hydrogen bonds can increase the chemical bonding and intermolecular forces of the main chain, resulting in increased tensile strength. In addition to the molecular structure, the mechanical properties of PI depend on the synthesis method and processing conditions. The thermal history during the formation of PI affects its aggregate state structure, which ultimately has an impact on the mechanical properties.

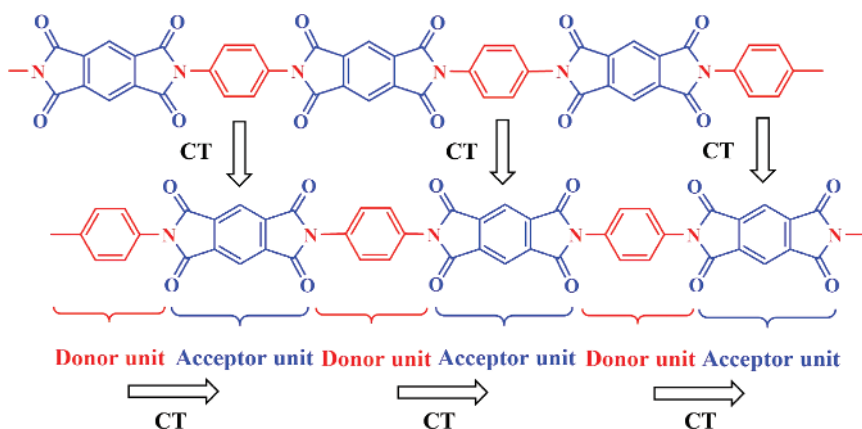


Figure 1.1 Intermolecular and intramolecular charge transfer (CT) in PI.
Source: Ref. [3]/Springer Nature.

The electrical properties of polymers refer to the behavior of polymers under the action of an applied voltage or electric field and the various physical phenomena they exhibit. PI is a typical linear dielectric with excellent dielectric and insulating properties. The dielectric permittivity of PI is mainly contributed by dipolar polarization of their polar groups. Therefore, the introduction of polar groups into the PI molecular chain, or an appropriate increase in free volume can improve the dielectric permittivity of PI. For instance, Liu et al. [4] introduced polar groups $-\text{COOH}$ and $-\text{CO-NH-}$ into the PI main chain by controlling the degree of imidization of PAA (Figure 1.2), resulting in a dielectric permittivity up to $4.59@1\text{ kHz}$. However, the promotion strategies of dielectric permittivity usually lead to a higher dielectric loss. Thus, systematic consideration of the molecular/structure design according to the polarization mechanisms is necessary to improve the dielectric loss of PIs. The insulating properties of PIs depend mainly on the bandgap and carrier traps. Wang et al. [5] found that the high-temperature insulation performance would experience diminishing marginal utility as the bandgap increases beyond a critical point ($\sim 3.3\text{ eV}$) through the study of some series of PI derivatives. Therefore, it is essential to ensure a wide bandgap while constructing deep traps to enhance the insulation performance of PI [6]. There are three strategies for constructing carrier traps: adjusting the intrinsic structure of polymers, preparing inorganic/polymer composites and all organic polymer composites.

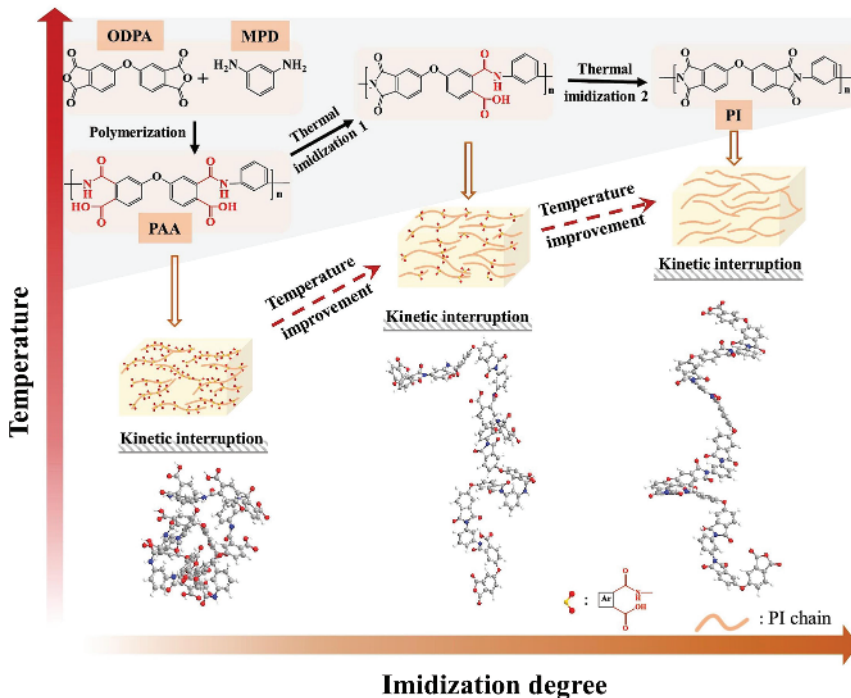


Figure 1.2 Schematic diagram of the thermal imidization process of PAA. Source: Adapted from Ref. [4].

1.3 Fabrication of Polyimide

PI boasts of numerous synthetic pathways and can be tailored for diverse applications, making it unparalleled among other polymers [7]. PIs are generally synthesized by a two-step process. Firstly, polyamic acid (PAA) is obtained by low-temperature polycondensation of dianhydride and diamine in a polar solvent (N, N-dimethylacetamide, N, N-dimethylformamide, and N-methylpyrrolidone). Subsequently PAA can be thermally or chemically dehydrated to obtain PI. PI can also be synthesized in one step, where the dianhydride and diamine are polycondensed by heating in a high boiling solvent (phenolics). The monomer ratio, dosing sequence, and reaction temperature are the core parameters affecting the PI polymerization reaction. For example, the ring-opening polymerization of dianhydride and diamine is an equilibrium reaction and has a high equilibrium constant, with the reaction heavily biased in favor of the product [8]. The polymerization process is significantly exothermic, and a proper lowering of the reaction temperature is more conducive to a positive reaction.

After decades of development, PI can be processed by methods suitable for most polymers. For example, PAA solutions can be utilized for cast film formation, spin coating, and spinning. Because inorganic salts are not generally produced during the synthesis of PI, there is no need for an additional purification step, which is very favorable for the preparation of insulating materials. PI can also be thermo-compressed, extruded, and injection molded by melt processing. Moreover, it is possible to utilize the easy sublimation of dianhydride and diamine for vapor-phase deposition. The diverse range of processing technologies employed by PI enables the production of a multitude of materials, including films, fibers, foams, and adhesives.

1.4 Applications of Polyimide

PI, a high-performance polymer, enjoys widespread utilization across various industries owing to its exceptional structural properties, facile synthesis process, and adaptability to diverse processing techniques. Its unique chemical and physical characteristics have allowed it to demonstrate outstanding performance in a broad range of applications, as shown in Figure 1.3 [9]. Each of these applications, from aerospace and automotive components to medical implants and semiconductor devices, has benefited from PI's ability to deliver superior performance in challenging environments. Consequently, PI continues to be a highly sought-after material for a diverse range of applications worldwide.

1.4.1 Capacitive Energy Storage

PI has a very broad application prospect in the field of dielectric energy storage. There is now a high demand for polymer dielectrics with outstanding high-temperature capacitance performance [10]. Because in many areas, such as

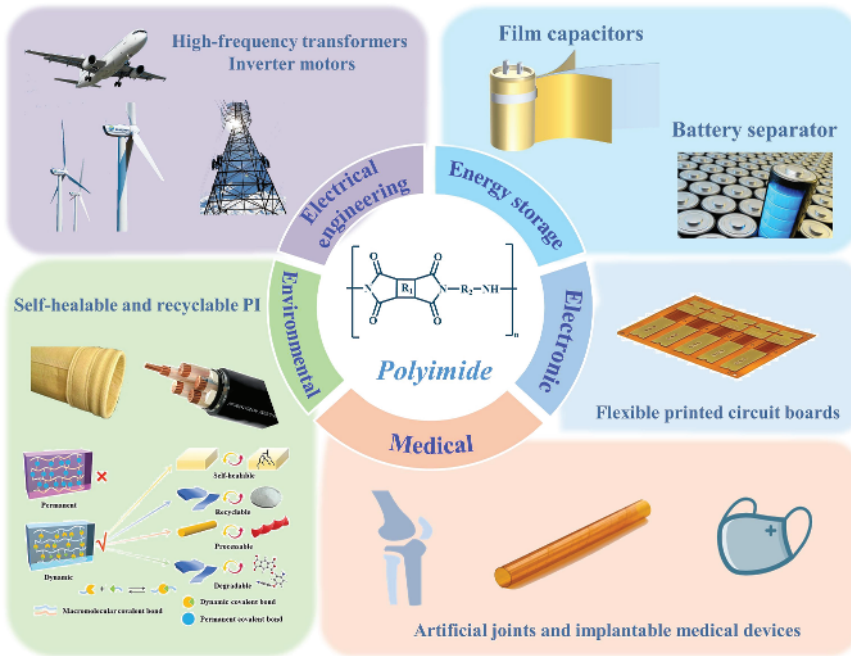


Figure 1.3 Applications of polyimide. Source: Ref. [9]/John Wiley & Sons.

hybrid electric vehicles, underground oil/gas exploration, and aircraft electrification, film capacitors typically operate at high temperatures ($>150^\circ\text{C}$) [11]. However, the maximum operating temperature of commercially available biaxial-oriented polypropylene (BOPP) should not exceed 105°C [12]. PI is considered to be the most promising material for high-temperature energy storage. Therefore, many researchers have carried out studies in order to improve the usage of PI in high-temperature energy storage applications [13, 14]. In addition to physical energy storage, PI can be used in the new energy field to manufacture high-performance battery separators and fuel-cell bipolar plates.

1.4.2 Electronic Devices

As an important interlayer dielectric material for flexible copper-clad laminate, PI film plays a crucial role as the structural and functional basis for flexible printed circuit boards. However, the dielectric permittivity of PI is about 3.4, which is no longer sufficient to meet the needs of integrated circuits process development. In order to reduce the dielectric permittivity of PI, researchers have carried out a lot of modification work on PI from the Clausius–Mosotti equation. The dielectric permittivity of PIs can be effectively reduced by introducing fluorine atoms, bulky side groups, or porous structures [15]. Moreover, designing dielectrics with low permittivity and high thermal conductivity is crucial to improve the signal transmission quality of smart terminals and effective heat dissipation of devices [16].

1.4.3 Electrical Engineering

PI is particularly suitable for use as a flexible printed circuit board substrate. For example, transparent polyimide films can be used to make flexible solar cell substrates. Moreover, PI is widely used as an insulating material for high-frequency transformers, inverter motors, and wind power generation equipment. However, the poor corona resistance of PI at high-frequency voltages seriously shortens the service life of electrical equipment. The addition of appropriate amounts of nanoparticles has been shown to be effective in improving the corona resistance of PI [17]. DuPont has developed a sandwich structure of 100 CR films (top and bottom layers are Al_2O_3 -doped PI composite films and the middle layer is a pure PI film), which provides higher corona resistance at high-frequency voltages, up to 10 times that of a pure PI film (100 HN) [18].

1.4.4 Medical Materials

PI has low toxicity and can be used as a multifaceted medical material. Certain PIs have high compatibility with blood and tissues, which is the reason for their interest in biocompatible material applications. For instance, PI can be used to make artificial joints, implantable medical devices, and biodegradable sutures.

1.4.5 Environmental Protection

The heat and organic solvent resistance of PI is particularly important in the separation of organic liquids and gases. High-temperature filtration materials prepared from PI fibers are widely used for exhaust gas treatment in cement production, steel, and other industries. In addition, PI has excellent stability and durability and maintains its original performance even in extreme environments, so it can be used for long periods of time without much maintenance or replacement. However, high T_g PI molecular chains are difficult to move at room temperature and cannot be actively recycled and self-healed after destruction. Self-healable and recyclable PIs have great practical engineering application value and environmental significance, promoting the development of a sustainable society. In recent years, a small amount of studies have been published to modulate the dynamic behavior of PI such as self-healable, recyclable, and degradable abilities by adjusting the structure of molecular chains and the composition of monomers [19, 20].

1.5 Summary and Outlook

In summary, PI can be used in many applications through the choice of structural design and synthetic processing methods. These areas include high-temperature energy storage, low dielectric, corona resistance, thermal conduction, electromagnetic shielding, optical transparency, corrosion resistance, and dynamics.

The primary reason that the PI has not become a more prevalent breed over the past half-century is its high cost. But from a chemical standpoint, the cost of PI can be

reduced. There are two main ways to reduce the cost, one is to develop new monomer synthesis and polymerization methods, and the other is to use PI to modify other polymers. As preparation technology continues to evolve and costs are reduced, PI is poised to assume a more prominent role in the field of materials in the future.

It can be predicted that the future development direction of PI will mainly focus on high performance, multifunctionality, environmental protection and sustainability, and the expansion of application areas. This will bring new opportunities and challenges for the development of polyimide materials, and at the same time will promote the progress and development of related fields.

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