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Main Research and Development Trends for Fluorine-Free CPI in Electronic Applications

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Abstract. With the rapid development of electronic information industries such as flexible displays, 5G/6G communications, and semiconductor packaging, colorless and transparent polyimide (CPI) has become an indispensable electronic substrate material due to its combination of high optical transmittance, excellent thermal stability, superior mechanical properties, and low dielectric characteristics. Traditional transparent polyimides typically incorporate fluorine atoms to inhibit the formation of intra- and intermolecular charge transfer complexes (CTC) to enhance transparency. However, fluorinated monomers face challenges including high costs, complex synthesis processes, and the demands of large-scale industrialization and green electronics development. Therefore, the development of fluorine-free transparent polyimide (FFPI) has emerged as a critical research direction in the field of electronic polymer materials. Centering on the raw material design and processing technologies of fluorine-free CPI, this paper reviews the regulation mechanisms of FFPI in terms of optical properties, thermal properties, dimensional stability, and dielectric properties. It also identifies current bottlenecks in FFPI regarding the balance of performances and processing stability. The paper serves as a reference for further research and process optimization of fluorine-free transparent polyimides in the electronics sector.

Keywords: Fluorine-free CPI, Transparent polyimide, Electronic materials, Raw material design, Processing technology

1. Introduction

The rapid iteration of flexible displays, high-frequency circuits, and advanced packaging has driven the upgrade of electronic substrate materials toward high transparency, high-temperature resistance, low dimensional change, and environmental friendliness. Colorless and transparent polyimide (CPI), by virtue of its excellent thermal stability, mechanical strength, and insulating properties, has become a core material for flexible OLED substrates, foldable screen cover films, and dielectric layers for high-frequency flexible printed circuits (FPC). Traditional CPI largely relies on fluorinated monomers to inhibit intramolecular charge transfer to enhance optical transmittance. However, issues arising from fluorine elements, including persistent environmental pollution, weak interfacial adhesion, and poor process compatibility, have become increasingly prominent. Driven by the dual requirements, the development of fluorine-free CPI with high transparency, high thermal stability, and low dielectric loss has become a research hotspot in the fields of polymer materials and electronic information.

Current research on fluorine-free CPI mainly focuses on strategies such as alicyclic monomers, non-coplanar backbones, bulky side groups, and asymmetric copolymerization, aiming to reduce conjugation and molecular packing density, thereby improving thin-film transmittance and inhibiting yellowing. Simultaneously, the electronics sector imposes more stringent requirements: visible light transmittance must exceed 85%, the glass transition temperature (Tg) must surpass 300°C, the coefficient of thermal expansion (CTE) must match silicon wafers and metal circuitry, and the high-frequency dielectric constant and loss must meet the needs of 5G/6G communication. These performance demands make the synergistic optimization of raw material selection and film-forming processes critical to breaking through technical bottlenecks.

Accordingly, this paper summarizes the R&D directions of fluorine-free CPI from the two major dimensions of raw material systems and processing technologies. It outlines key technical bottlenecks and development trends, providing a theoretical reference for the development of green substrates for flexible electronics.

2. R&D directions of fluorine-free CPI raw material systems

2.1. Molecular design of fluorine-free dianhydride and diamine monomers

Due to their saturated cyclic backbones, alicyclic structures effectively prevent conjugation pathways, leading to colorless transparency. However, rigid alicyclic structures often lead to excessive polymer chain rigidity, which reduces solubility and increases brittleness. Furthermore, alicyclic structures exhibit inferior thermal stability compared to aromatic structures [1]. Research indicates that copolymerizing six-membered alicyclic dianhydrides with flexible alicyclic diamines can effectively regulate the rigidity and flexibility of molecular chains. Kim et al. systematically compared fluorinated and fluorine-free CPI nanocomposite systems, confirming that the fluorine-free route offers superior advantages in environmental friendliness, interfacial adhesion, and thermal cycling reliability; however, achieving a balance between high transparency and a low coefficient of thermal expansion (CTE) remains a challenge [2]. Kwon et al. prepared a series of colorless transparent CPI films by introducing alicyclic monomers containing ether bonds. While maintaining high optical transmittance, they significantly improved the flexibility and folding reliability of the films, providing a raw material solution for flexible display cover applications [3].

By introducing twisted structures or bulky side groups into the molecular backbone, the regularity of the polymer chains is disrupted, reducing intermolecular packing density. This reduces light scattering and enhances solubility. This structural regulation strategy does not require sacrificing thermal stability, making it a preferred solution for balancing multiple properties. For example, diamine monomers containing 9,9'-diphenylfluorene structures can effectively hinder close packing of chain segments due to their massive steric hindrance. Qi et al. introduced bulky side groups into a fluorine-free CPI system, achieving high transmittance across the entire visible spectrum while significantly reducing the material's water absorption and dielectric constant through side-group cross-linking effects. This provided an ideal raw material selection for high-frequency communication substrates [4].

In the absence of the strong electron-withdrawing effect of fluorine atoms, designing monomers based on the principle of weak electron donor-acceptor (D-A) matching is key to inhibiting the CTC effect. By selecting monomer combinations with high oxidation potentials and low reduction potentials, the energy gap between frontier molecular orbitals is increased, thereby reducing exciton formation and decreasing light absorption. Current research trends focus on introducing low-polarity ortho-substituted groups, such as heterocyclic monomers containing sulfur or silicon. The moderate electronegativity of these atoms allows for the regulation of electron cloud distribution while introducing hydrophobic characteristics. This improves the dielectric stability of fluorine-free CPI in humid environments, which is crucial for meeting the high-humidity reliability tests of electronic devices [5].

2.2. Greenness and high purification of electronic-grade solvent systems

As the medium for polymerization, solvents serve as a critical factor influencing the insulation performance and reliability of electronic-grade CPI due to their residues. Traditional CPI synthesis relies on strong polar aprotic solvents such as N,N-dimethylacetamide (DMAc) and N-methylpyrrolidone (NMP); however, these solvents exhibit reproductive toxicity and are difficult to remove completely [6].

Current R&D is focusing on photoresist-compatible solvents such as propylene glycol methyl ether acetate (PGMEA) and γ-butyrolactone (GBL). These solvents not only possess lower toxicity but have an inherent compatibility with semiconductor manufacturing processes, thereby reducing the difficulty of subsequent process adaptation [7]. However, the polarity of green solvents is often insufficient to dissolve highly rigid fluorine-free polyamic acid (PAA) precursors. Consequently, mixed solvent systems has emerged as a compromise: using a small amount of high-polarity solvent as a co-solvent paired with a primary green solvent to meet environmental and process requirements while ensuring solubility.

For electronic applications, the metal ion content in solvents must be controlled at the ppb (parts per billion) level. When procuring raw materials, "electronic-grade" or "MOS-grade" must be specified, and molecular sieve dehydration followed by vacuum distillation must be performed prior to use. Residual metal ions (such as Na^+,K^+,Cl^-) act as charge carrier traps, reducing the insulation resistance of the material and potentially leading to device leakage failure. Therefore, solvent purification technology represents an invisible threshold for fluorine-free CPI to enter the electronics supply chain.

2.3. Functional additives and nanocomposite reinforcement systems

Pure resin systems often struggle to simultaneously meet all the stringent requirements of the electronics field (such as extremely low CTE, high thermal conductivity, and low dielectric constant). Consequently, composite modification through the addition of functional additives and nanofillers has become the mainstream R&D direction in the industry.

Due to their high surface energy, fluorine-free CPIs exhibit relatively poor interfacial compatibility with inorganic fillers. The introduction of silane coupling agents (e.g., KH-560) or titanate coupling agents can establish a "molecular bridge" between the organic matrix and inorganic fillers, preventing filler agglomeration and enhancing the mechanical properties and dimensional stability of the films. Additionally, to address the susceptibility of fluorine-free systems to thermal oxidative degradation during high-temperature imidization, the addition of hindered phenolic or phosphite antioxidants can effectively inhibit yellowing, ensuring the retention of optical properties after high-temperature processing.

To adapt to 5G/6G high-frequency and high-speed applications, reducing the dielectric constant (Dk) is a core objective. Currently, mainstream fillers include hollow silica (HSiO2), fluorinated graphene (used in trace amounts to avoid disrupting the fluorine-free matrix), and polyimide microspheres. The air phase (Dk≈1) introduced by the hollow structures can significantly lower the overall dielectric constant of the composite material. Regarding dimensional stability, adding fillers with negative thermal expansion coefficients, such as boron nitride (BN) or talc, can offset the positive thermal expansion of the polyimide matrix through physical compounding. This can reduce the CTE to below 10 ppm/°C, matching the thermal expansion characteristics of copper foil and silicon wafers, thereby resolving warpage issues in flexible printed circuits.

The greatest challenge currently facing the R&D of fluorine-free CPI raw materials lies in the multi-objective synergy of performances; transparency, mechanical strength, and processing ease often cannot be optimized simultaneously. Future R&D directions will focus on molecular-level composites and in-situ polymerization techniques. By introducing fillers directly during the polymerization process to achieve atomic-level uniform dispersion, specific key indicators can be precisely enhanced without significantly sacrificing other properties.

3. R&D directions for fluorine-free CPI processing technology

The development of precise, controllable, and continuous processing technologies centered on electronic application scenarios is the core link in transforming fluorine-free CPI from laboratory samples into electronic-grade thin-film products.

3.1. Precursor preparation and polymerization processes

The quality of the polyamic acid (PAA) precursor is the foundation that determines the uniformity, defect levels, and final performance of fluorine-free CPI films. The polymerization process directly affects the precursor's molecular weight, molecular weight distribution, viscosity stability, and shelf life. Fluorine-free CPIs predominantly utilize alicyclic and non-coplanar dianhydride and diamine monomers, whose reactivity and solubility differ significantly from traditional aromatic monomers. Consequently, precise control over the low-temperature solution polycondensation process is required [8].

Low-temperature solution polycondensation is the most mainstream process for preparing fluorine-free CPI precursors. Core control parameters include polymerization temperature, reaction time, solid content, stirring rate, and feeding sequence. Fluorine-free monomers typically undergo polycondensation within a temperature range of -10 to 5°C. A low-temperature environment suppresses side reactions, prevents cross-linking and branching, and ensures the structural regularity of the PAA segments [9]. The reaction endpoint is determined through online viscosity monitoring to ensure the molecular weight reaches the target range. Solid content is a key indicator for adapting to subsequent film-forming processes; while laboratory preparation often employs a solid content of 10%–15%, roll-to-roll (R2R) continuous film forming requires an increase to 18%–25% to ensure fluidity while reducing dimensional shrinkage caused by solvent evaporation.

Direct polycondensation eliminates intermediate separation steps, thereby shortening the process and reducing costs, but it imposes stricter requirements on anhydrous/oxygen-free environments and monomer purity. Conversely, the soluble PI route achieves direct dissolution of the resin in organic solvents through molecular design, bypassing the PAA stage. This avoids issues such as incomplete imidization and high residual stress at the source, making it better suited for high-precision electronic film processing, though it carries the risk of decreased thermal resistance and dimensional stability. In terms of industrialization, the transition from batch polymerization to continuous tubular polymerization is the prevailing trend. Continuous processes allow for precise and stable control of temperature, concentration, and residence time, significantly improving the consistency between different batches and meeting the high stability requirements of electronic materials.

3.2. Film-forming processes for electronic thin films

Film forming is the core process for achieving the thin-film transition and high precision of fluorine-free CPI. The electronics sector imposes extremely high requirements on thickness uniformity, surface roughness, defect density, ultra-thin profiles, and large-scale dimensions, making traditional batch film-forming methods inadequate for industrial demands. Current fluorine-free CPI film-forming processes center on solution coating, primarily encompassing four technical routes: solution casting, slot-die coating, blade coating, and roll-to-roll (R2R) continuous film forming.

Roll-to-roll (R2R) continuous film forming is the hallmark of fluorine-free CPI industrialization. It enables integrated, continuous production across unwinding, coating, pre-drying, imidization, curing, and winding, significantly enhancing production efficiency and material utilization. The electronics field has set clear requirements for the ultra-thinning of fluorine-free CPI films; however, issues arising from ultra-thinning—such as surface pinholes, film breakage, and uneven tension—present significant challenges for process control. Simultaneously, large-scale production (widths≥1000mm) and low-defect control are the primary focuses of film-forming R&D. These goals necessitate the use of optimized die heads, airflow control, enhanced cleanliness, and online inspection systems to reduce defects such as particles, fish-eyes, and streaks.

3.3. Imidization processes

Imidization is the core reaction involving the dehydration and cyclization of PAA segments to form imide rings. it directly determines the optical transmittance, yellowness index (YI), thermal stability, mechanical properties, and dimensional stability of fluorine-free CPI, making it the most critical stage in the processing workflow affecting final product quality. Current mainstream processes are categorized into three types.

Thermal imidization is the most widely used route in industrial applications, achieving dehydration and cyclization through programmed heating. Core control parameters include the heating rate, final temperature, holding time, atmospheric environment, and vacuum assistance [10]. Thermal imidization of fluorine-free CPI typically employs a stepwise heating profile, gradually increasing from 80°C to 250–350°C. During this process, solvents are removed in the low-temperature stage, cyclization is initiated in the mid-temperature stage, and full imidization along with residual stress relaxation is completed in the high-temperature stage [11]. Nitrogen protection and vacuum assistance can effectively inhibit high-temperature yellowing and enhance film transmittance. However, pure thermal imidization suffers from slow cyclization rates, prolonged exposure to high temperatures, high dimensional shrinkage, and significant residual stress, which can easily lead to film curling and warpage.

Chemical imidization utilizes the synergistic effect of dehydrating agents and catalysts to achieve complete cyclization under low-temperature conditions ranging from room temperature to 100°C. This fundamentally avoids high-temperature thermo-oxidative yellowing, significantly enhancing the optical properties of fluorine-free CPI while substantially reducing dimensional shrinkage and improving dimensional stability. Commonly used dehydrating agents include acetic anhydride, while catalysts include pyridine and triethylamine. This process is better suited for display-grade CPI, which requires extreme transparency and low stress [10].

3.4. Post-treatment and functional modification

Post-treatment is the final stage for optimizing the comprehensive performance of fluorine-free CPI and achieving functional adaptation for electronic scenarios. By employing physical or chemical means to regulate the internal stress, surface properties, thermal characteristics, and barrier performance of the film, it resolves contradictions between transparency, dimensional stability, interfacial adhesion, and environmental endurance.

Thermal annealing and tensile orientation are the core methods for regulating the coefficient of thermal expansion (CTE). Due to the relatively high flexibility of their molecular chains, the pristine CTE of fluorine-free CPI is typically high, leading to poor compatibility with electronic components such as copper foil, glass, and ITO. High-temperature annealing after imidization can further release residual stress and stabilize the molecular chains. Furthermore, uniaxial or biaxial tensile orientation can align molecular chains orderly along the planar direction, reducing the CTE from 20–40 ppm/°C to below 10 ppm/°C, thereby meeting the dimensional stability requirements of high-temperature manufacturing processes [12].

Plasma, corona, and ultraviolet (UV) modifications are mainstream technologies for enhancing interfacial adhesion. Fluorine-free CPI possesses low surface energy and high chemical inertness, resulting in poor bonding strength with materials like copper foil, photoresist, and ITO transparent electrodes, which often leads to delamination. Low-pressure plasma or corona treatments can introduce polar groups such as hydroxyl and carboxyl groups onto the film surface, increasing surface energy and wettability. UV modification combines surface etching with the introduction of functional groups; this process is more environmentally friendly and controllable, making it well-suited for the interfacial connection requirements of flexible displays and flexible circuits.

Surface densification and composite water/oxygen barrier layers are utilized to enhance the environmental stability of fluorine-free CPI. By preparing ultra-thin oxide layers on the CPI surface through methods such as sol-gel coating or atomic layer deposition (ALD), water absorption and gas permeability can be reduced. This extends the lifespan of devices in high-temperature and high-humidity environments, satisfying the reliability requirements for automotive displays and outdoor flexible electronics.

3.5. Processing technology bottlenecks

Although fluorine-free CPI processing technologies have achieved breakthroughs from the laboratory to pilot-scale production, several core bottlenecks remain for large-scale electronic-grade mass production. During the film-forming and imidization stages, issues such as film curling and warpage caused by the incomplete release of residual stress are prominent, particularly in ultra-thin films. Uneven solvent evaporation and insufficient leveling tend to produce defects such as pinholes and shrinkage cavities, which reduce the yield of electronic devices. Furthermore, yellowing and the decline in optical transmittance caused by high-temperature imidization make it difficult to achieve ultra-high transparency targets, such as a Yellowness Index (YI) < 1.5 [13].

On an industrial level, the stability of roll-to-roll continuous processes remains insufficient, with key technologies such as width expansion, tension control, and temperature field uniformity still requiring breakthroughs. Consistency in thickness, optical, thermal, and mechanical properties across different batches of films is poor, failing to meet the standardization requirements for electronic materials. Simultaneously, the compatibility of high-solid-content, low-viscosity precursor systems is inadequate, and the costs associated with solvent recovery and environmental treatment are high, leading to a relatively low level of green manufacturing. These processing bottlenecks directly restrict the large-scale application of fluorine-free CPI in fields such as high-end flexible displays, high-frequency/high-speed circuits.

4. Conclusion

This paper reviews the current status and technical bottlenecks of fluorine-free CPI in terms of raw material selection and processing technologies. However, the literature coverage in this review remains limited and does not fully represent the entirety of the latest global research progress and technical roadmaps for fluorine-free CPI. Future work could further expand the scope of literature retrieval to enhance the comprehensiveness and cutting-edge nature of the review.

Future R&D for fluorine-free CPI will focus on breakthroughs across four dimensions. In terms of molecular design, leveraging AI-assisted structure-property relationship analysis to construct modular copolymerization systems will allow for the precise regulation of molecular chain structures, aiming to achieve the synergistic optimization of transparency, thermal stability, and dielectric properties. Regarding green manufacturing, research will focus on solvent-free or water-based preparation processes, high-efficiency solvent recovery technologies, and low-temperature imidization schemes to minimize environmental impact, aligning with the green development trends of the electronics industry. In the field of functional integration, the development of fluorine-free CPI composite films with transparent conductivity, self-healing, flame retardancy, and biocompatibility will expand their use in emerging scenarios such as flexible wearables and biomedical electronics. At the application level, further cultivation of fields such as automotive displays, photovoltaic modules, and advanced packaging is essential.

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