

Recent Developments on the Synthesis of Colorless Polyimides

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Abstract

Driven by the rapid advancement of transparent and flexible electronic technologies, colorless polyimides (CPIs) have emerged as an important class of high-performance polymeric materials. In recent years, the increasing demand for lightweight, flexible, and optically transparent substrates for advanced optoelectronic devices has stimulated extensive research on CPI materials. Compared with conventional aromatic polyimides, which generally exhibit deep coloration due to strong intermolecular charge-transfer interactions, CPIs are specifically designed to achieve high optical transparency while retaining the outstanding thermal, mechanical, and chemical resistance characteristics intrinsic to polyimides. Owing to these unique properties, CPI films have found potential applications in flexible displays, foldable smartphones, organic light-emitting diode (OLED) devices, solar cells, touch panels, flexible printed circuit boards, and other next-generation electronic systems. Recent developments in CPI research have primarily focused on molecular design strategies aimed at suppressing charge-transfer complex formation without significantly compromising thermal stability and dimensional integrity. Various structural modifications, including the incorporation of fluorinated groups, bulky substituents, asymmetric moieties, alicyclic units, and non-coplanar rigid structures, have been widely explored to improve optical transparency and solubility. At the same time, considerable attention has been devoted to maintaining high glass transition temperatures, low coefficients of thermal expansion, and excellent thermo-mechanical properties required for advanced device fabrication processes. This chapter reviews the recent synthesis of CPIs and outlines future prospects, focusing on recent developments in novel monomer design and their influence on the thermal and optical properties of the resulting polyimides.

Keywords: *Charge-Transfer Interactions; Colorless Polyimides (CPIs); Flexible Optoelectronic Devices; Optical Properties; Thermal Properties*

Introduction

Over the past two decades, colorless and optically transparent polymers have found significant applications in touch panels, flexible displays, organic photovoltaics, optical films, flexible printed circuit boards, and other advanced flexible optonic devices, where glass substrates were traditionally used. In recent years, the demand for flexible and transparent materials coated with conductive oxides (Indium Tin Oxide) has further increased, particularly in display technologies and microelectronics.

However, ITO-based systems suffer from several limitations. Indium is a rare and costly element and achieving high-quality ITO (Indium Tin Oxide) coatings typically requires high-temperature processing, especially when deposited on glass substrates. In addition, glass itself is inherently brittle and lacks flexibility, making it unsuitable for next-generation flexible devices (Choi *et al.*, 2010). Replacing conventional fragile inorganic glass substrates (typically 400–700 μm thick) with much thinner plastic substrates (less than 50 μm) can make display devices lighter, more durable, and highly flexible.

Many polymer optical films are recently applied in the fabrication of different flexible smart optonic devices. For this purpose, optical polymer films must meet several critical requirements such as glass transition temperature above 300 °C, high transparency in UV-Vis region, high processability, sufficient film flexibility, excellent mechanical properties, roll-to-roll (R2R) compatible, compatibility with film-forming processes,

resistance to solvents, and a low coefficient of thermal expansion (CTE). Among these, maintaining high optical transparency at very high processing temperatures is most important. For example, in the fabrication of next-generation flexible thin-film transistor (TFT)-driven active-matrix liquid crystal display (TFT-LCD) devices and flexible active-matrix organic light-emitting diode (AMOLED) displays, polymer film substrates are often exposed to demanding thermal conditions, with processing temperatures exceeding 300°C. In addition, key photoelectric fabrication techniques, such as physical vapor deposition (PVD) and plasma-enhanced chemical vapor deposition (PECVD), typically involve even higher temperatures, which can surpass 400°C (Liu *et al.*, 2017). Such elevated processing temperatures impose stringent requirements on substrate materials. However, most conventional optically transparent plastic substrates are not designed to withstand these harsh conditions. As a result, they tend to suffer from thermal deformation, loss of optical transparency, and degradation of mechanical strength, making it difficult to maintain their desired performance during device fabrication.

Based on their glass transition temperature (T_g), polymer-based optical films can be broadly categorized into three groups: conventional optical films ($T_g < 100^\circ\text{C}$), intermediate or common high-temperature optical films ($100^\circ\text{C} \leq T_g \leq 200^\circ\text{C}$), and high-temperature optical films ($T_g > 200^\circ\text{C}$), as illustrated in Figure 1. This classification highlights the thermal limitations of different polymer systems in relation to their suitability for advanced optoelectronic applications.

Although several commercially available colorless super-engineering plastics exhibit excellent optical transparency, their glass transition temperatures are generally inadequate for high-temperature processing environments. For instance, poly(ethylene terephthalate) (PET) possesses a T_g of approximately 78°C, poly(ethylene naphthalate) (PEN) around 120°C, polycarbonate (PC) about 145°C, and poly(ether sulfone) (PES) near 225°C (Figure 2). These T_g values remain significantly below the thermal demands of modern device fabrication processes. In particular, processes such as lead-free solder reflowing, which typically occur at temperatures around 270°C, and silicon-based thin-film transistor (TFT) fabrication, which can involve short-term exposure to temperatures approaching 400°C, exceed the thermal tolerance of these materials. Consequently, such polymers are unable to maintain their structural integrity and functional performance under these harsh processing conditions, thereby limiting their applicability in next-generation flexible electronic and optoelectronic devices (Yang & Yuan, 2018).

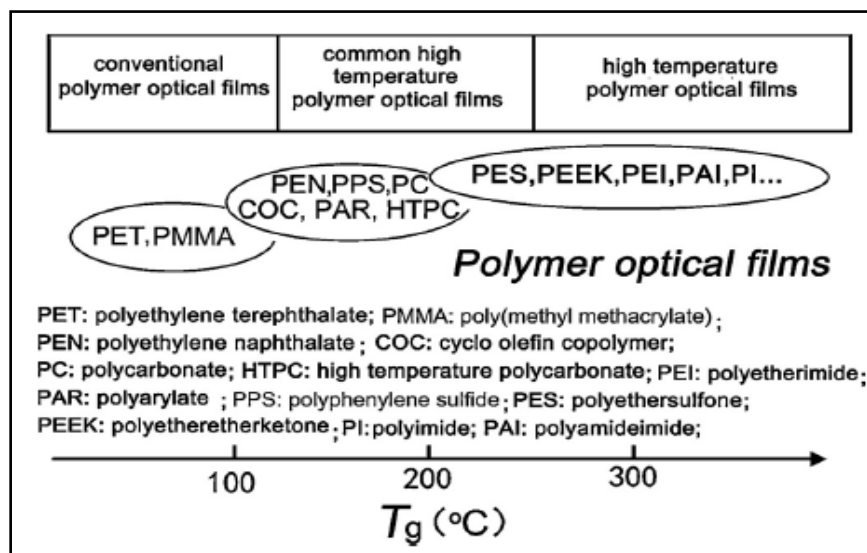


Figure 1: Glass Transition Temperature (T_g) of Polymer Films Used in Optical Devices (Yang & Yuan, 2018)

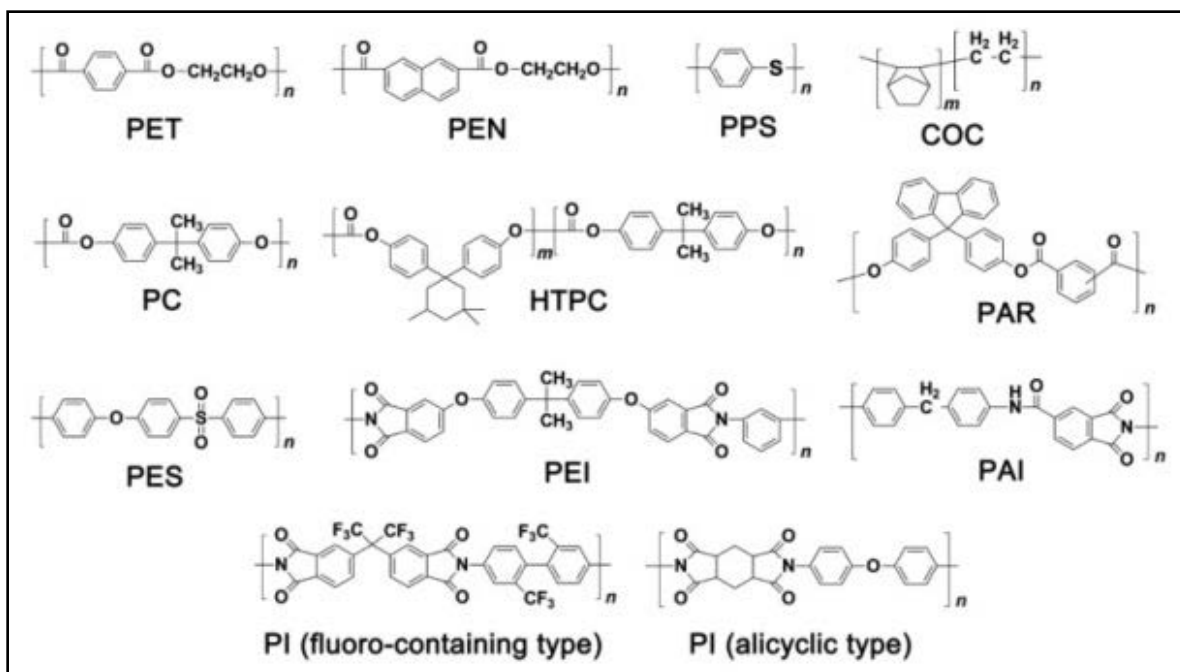


Figure 2: Chemical Structures of Various Polymer Optical Films (Liu et al., 2015)

The rapid advancement of optoelectronic technologies has driven the demand for polymeric materials that combine high optical transparency with excellent thermal, mechanical, and processing properties. Among high-performance polymers, polyimides (PIs) and probenazole's exhibit sufficiently high glass transition temperatures (T_g); however, the practical application of colorless probenazole's is limited by issues such as poor processability, availability of very few monomers, complex synthetic methodologies and manufacturing requirements (Tapaswi & Ha, 2019).

In contrast, colorless polyimides (CPIs) dominate the field; accounting for the majority of optically transparent polymer films (Yi et al., 2020). Colorless polyimides (CPIs) are widely utilized across advanced flexible electronic applications. They serve as (i) base substrates for foldable and flexible display panels, including OLEDs, enabling high-definition, transparent, and mechanically robust bendable devices; (ii) substrates in flexible perovskite solar cells and organic photovoltaics (OPVs), where high optical transmittance and excellent flexural durability are essential; and (iii) materials for flexible printed circuit boards (PCBs) and sensor platforms that demand exceptional thermal stability (typically $T_g > 300^\circ\text{C}$), particularly in automotive and aerospace applications. Their widespread use is attributed to their balanced optical, thermal, dielectric, and mechanical performance, along with their structural tunability through molecular design. Consequently, CPIs are extensively utilized in advanced optoelectronic applications, including flexible electronic substrates.

Polyimide (PI) is basically a condensation polymer of carboxylic dianhydrides and diamines. All polyimides possess highly stable heterocyclic imide ring system. It has become the most popular high-performance polymer in last two decades because of its outstanding thermal and chemical stability, excellent mechanical properties. PI offers outstanding promise for the high technology applications in the future. Polyimides (PIs) are widely used in aerospace, electronics, energy devices, membranes, sensors, and composite materials (Zhuang et al., 2019).

Polyimide (PI) chemistry dates back to 1908 with its initial synthesis from 4-aminophthalic acid, but major progress occurred in 1955 when high-molecular weight aromatic PIs were prepared via a two-step polycondensation of pyromellitic dianhydride (PMDA) with aromatic diamines (Mittal, 2007). This

breakthrough enabled large-scale development, leading to the commercialization of PMDA-ODA-based PI films in the early 1960s, with a trade name of Kapton® known for their exceptional thermal stability (T_g up to 385°C) and widespread use in flexible electronics and aerospace systems. Two other commercially successful thermally stable PI films are Novax™ and Upilex-S™. Further advancements followed with the introduction of other thermally robust PI films and the development of aliphatic and alicyclic PIs in the early 1970s (Lee *et al.*, 1971). Since then, a wide range of polyimides has been developed to take advantage of their excellent overall performance and versatility.

The outstanding thermo-mechanical stability of polyimides primarily arises from the presence of heterocyclic imide rings in their backbone. Incorporation of aromatic rings, either in the main chain or side chain significantly enhances the thermo-mechanical stability of aromatic polyimides. It has been well established that charge transfer complexes (CTCs) form between electron-donating diamine moieties and electron-withdrawing dianhydride units along the polyimide chain. These interactions tightly bind the polymer chains, restricting segmental motion, leading to a high glass transition temperature (T_g). Consequently, CTC formation largely accounts for the superior thermal, mechanical, and dielectric properties, as well as the excellent chemical resistance of polyimides, albeit at the cost of reduced solubility and increased processing difficulty.

Unfortunately, most of the aromatic PI films are deep in colors (brown, yellowish brown or amber) with poor optical transmittance (Tan *et al.*, 2020). Hence, these aromatic PIs cannot be used as optical transparent polymer in microelectronic and optoelectronic devices, as they fail to provide the required colorless transparency (Crawford, 2005). The deep color of conventional aromatic PIs is mainly, due to the intra- and inter-molecular charge-transfer (CT) interactions (Figure 3). The charge transfer complexes (CTCs) in PIs are formed due to the electronic transition between the highest occupied molecular orbital (HOMO) of the diamines and the lowest unoccupied molecular orbital (LUMO) of the dianhydrides. A larger HOMO-LUMO energy gap corresponds to absorption at shorter wavelengths, resulting in lighter-colored polyimide (PI) films. Suppression of CT interactions can be effectively achieved by reducing the electron-withdrawing strength of dianhydride moieties and the electron-releasing ability of diamine components (increasing the HOMO-LUMO energy gap), thereby improving the colorlessness of the PI films. Therefore, an effective strategy to obtain colorless polyimides (CPIs) is to employ weakly electron-withdrawing dianhydrides and/or weakly electron-donating diamines, thereby minimizing charge-transfer interactions (Guan *et al.*, 2014).

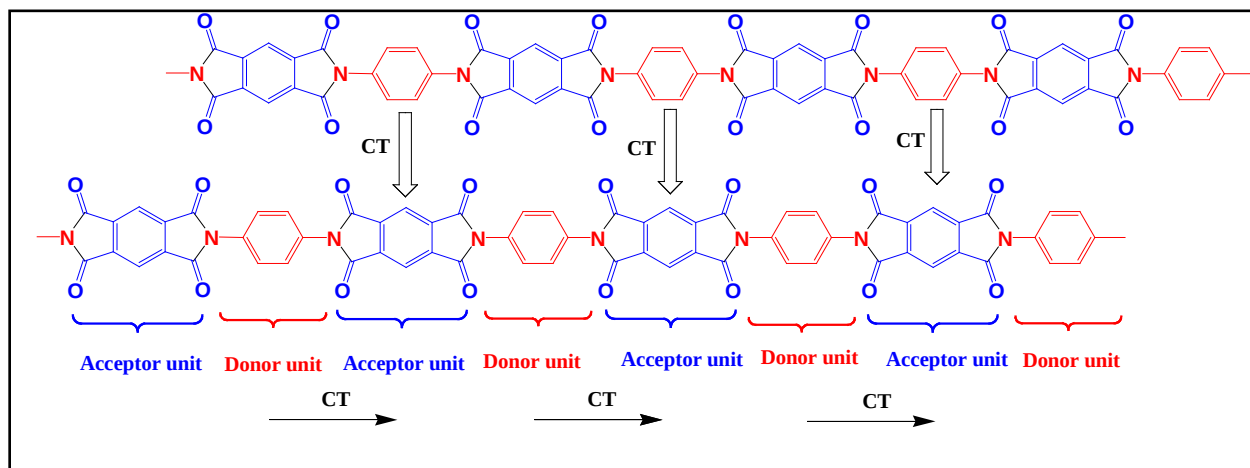


Figure 3: Charge-transfer Interactions in PI

The colorlessness of PI films is commonly evaluated using parameters such as light transmittance at 400 nm (T_{400}), the cutoff wavelength (λ_0 , defined as the wavelength at which transmittance becomes typically below 1%, the yellowness index (YI), which indicates the degree of coloration and haze (turbidity). Among

these parameters, T_{400} is arguably the most important factor for obtaining CPI. Although T_{450} or T_{500} values (transmittance measured at 450 or 500 nm) are commonly used to evaluate optical transparency, they do not necessarily guarantee the formation of truly colorless polyimides (PIs). In many cases, even when the transmittance at 500 nm (T_{500}) exceeds 80%, the polyimide film may still exhibit noticeable coloration (Itamura *et al.*, 1993). For films with a thickness of approximately 20 μm , $T_{400} > 80\%$, $YI < 3$ and haze below 1.0% ensures colorless appearance and is suitable for image display applications.

The optical transparency of polyimide films is mainly influenced by the monomer structure, synthetic approach (one-step or two-step), imidization method (chemical or thermal), and film processing conditions, including temperature, atmosphere, and solvent type. In wholly aromatic PIs, the main chains are composed of electron-donating diamine units and electron-accepting dianhydride units. Inter- and intrachain donor–acceptor CT interactions can generate an additional absorption band in the visible region, which leads to coloration in aromatic PI films. This behavior follows Mulliken's CT theory: $h\nu_{CT} (\propto \lambda_{CT}^{-1}) = IP - EA + C$ (1), where ν_{CT} is the frequency of CT absorption, IP is the ionization potential of the diamine, EA is the electron affinity of the dianhydride, and C is a constant. Since ν_{CT} is inversely proportional to the wavelength (λ_{max}) of the CT absorption band, reducing the EA of dianhydrides and increasing the IP of diamines raises the CT transition energy. This causes a blue shift (lower λ_{max}), thereby reducing the color intensity of PI films. To increase the ionization potential (IP) of diamines, electron-withdrawing groups such as $-\text{CF}_3$ and $-\text{SO}_2-$ or halogen atoms (e.g., Cl and F) are introduced into the aromatic diamine structure. Conversely, to decrease the electron affinity (EA) of dianhydrides, electron-donating groups such as $-\text{O}-$ can be incorporated. Again, inter-chain CT interactions can also be weakened effectively by introducing bulky groups (e.g., a cardo moiety), and aliphatic/alicyclic segments into backbones. It is now well recognized that introducing alicyclic substituents with low aromatic content—such as cyclobutene, cyclohexane, and cardo groups (e.g., diphenyl cyclohexane and adamantane)—as well as highly electronegative groups like trifluoromethyl ($-\text{CF}_3$) including the incorporation of fluorine atoms and $-\text{SO}_2$, or asymmetric and twisted rigid moieties, polymer chain packing can be disrupted considerably. These modifications effectively suppress CTC formation, leading to improved solubility, enhanced melt processability, and greater optical transparency in polyimides (PIs).

However, such improvements are often accompanied by a trade-off, as the thermo-mechanical stability of the materials tends to decrease. In contrast, the incorporation of highly conjugated and rigid aromatic structures, along with strongly polar, planar, or cross-linkable functional groups such as $-\text{CN}$, $-\text{OH}$, $-\text{CF}_3$, and acetylene, can markedly enhance thermal stability. This enhancement, however, is usually associated with increased coloration in the resulting polyimides. Consequently, achieving an optimal balance between solubility and optical transparency on one hand, and high thermo-mechanical stability on the other, remains a significant challenge.

To achieve highly transparent polyimides without sacrificing their outstanding thermal and mechanical characteristics, extensive molecular engineering approaches have been explored. Representative strategies involve the incorporation of bulky substituents, asymmetric moieties, and rigid yet non-coplanar structural units, along with the introduction of fluorinated groups and the utilization of alicyclic dianhydrides or diamines. Such molecular design strategies effectively weaken interchain interactions, inhibit dense chain packing, and disrupt extended π -conjugation, thereby suppressing the formation of CTCs, which are chiefly responsible for the coloration observed in conventional polyimides. As a result, such design approaches enable the development of colorless and transparent polyimides (CPIs) with significantly improved optical properties.

Classification of Colorless Polyimides

Based on the monomers used in their main chains, polyimides are broadly classified into aromatic and non-aromatic PIs. Non-aromatic PIs are further divided into semi-aromatic and fully aliphatic types (Figure 4 and

5). Aromatic PIs are made from both aromatic diamine and dianhydride monomers. Semi-aromatic PIs contain only one aromatic component, where either the diamine or the dianhydride is aromatic but the rest is aliphatic. Fully aliphatic PIs are composed of aliphatic or alicyclic diamine and dianhydride monomers.

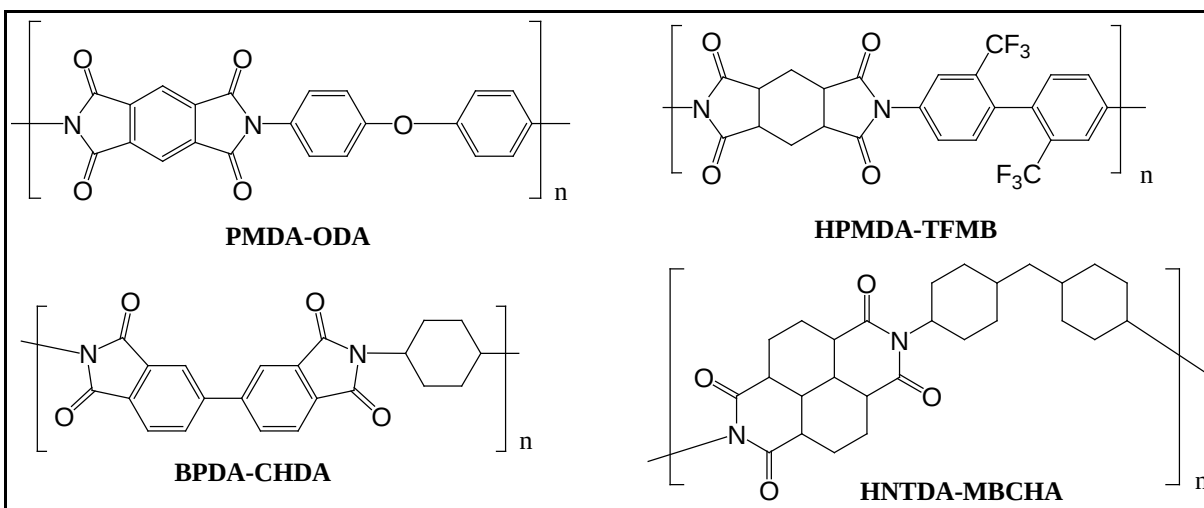


Figure 4: Different Kinds of PIs: Aromatic PI (PMDA-ODA), Semi Aromatic PIs (HPMDA-TFMB and BPDA-CHDA and Fully Aliphatic PI (HNTDA-MBCHA)

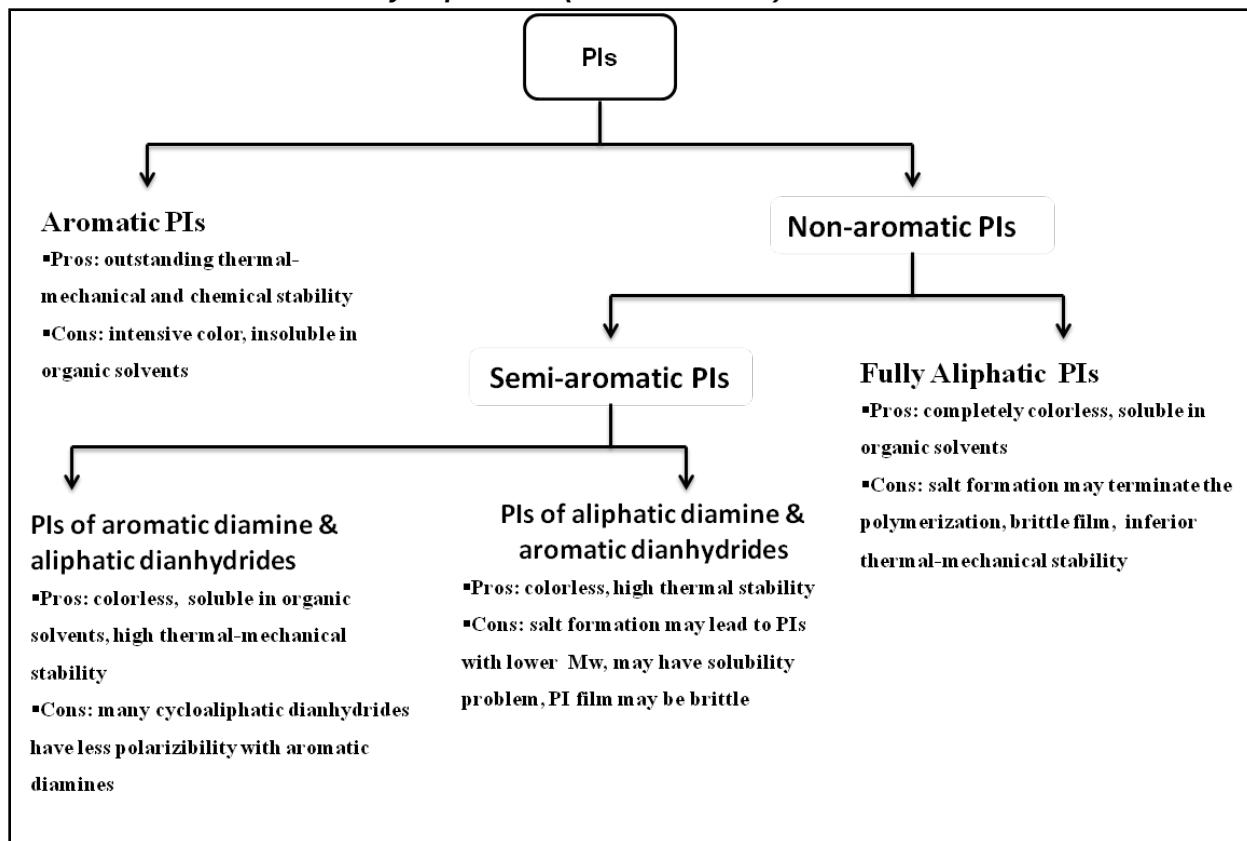


Figure 5: Different Kinds of PIs and Their Properties

Aromatic Colorless PIs

Aromatic polyimides represent one of the most extensively studied and commercially important classes of high-performance polymers. The typical examples of commercially successful aromatic PIs include Ultem® from G.E., DuPont's Kapton®, and Ube Industries Upilex®. Owing to their outstanding thermal stability, excellent mechanical strength, and superior electrical performance, these materials have been widely utilized as substitutes for metals and glass in advanced applications across the electronics, automotive, and aerospace sectors. The origin of many of these advanced thermo-mechanical and electronic properties of aromatic PIs is essentially due to the formation of strong CTC between dianhydride and diamine moieties. However, the presence of these CTC interactions also leads to significant coloration in PI films, thereby limiting their applicability in optoelectronic fields where high optical transparency and colorlessness are essential. In addition, aromatic PIs generally exhibit poor processability because of their limited solubility in common organic solvents. Furthermore, most conventional aromatic PIs possess relatively high dielectric constants, which restrict their application in low- κ dielectric materials. Consequently, despite their excellent overall performance, the practical application of aromatic PIs in advanced optoelectronic devices and high-speed multilayer printed circuit boards remain constrained by their poor solubility, high dielectric constant, and inherent yellow to dark-yellow coloration. To overcome these drawbacks, researchers have extensively modified the polymer backbone through various structural design strategies. These include incorporating flexible or asymmetric linkages, introducing non-linear features such as kinks, spiro or bulky groups, as well as cardo or pendant substituents, and utilizing fluorinated aromatic monomers. Such modifications help in developing polyimides that are colorless, more processable, and capable of retaining high thermal stability.

Most of the early-developed colorless polyimides were primarily derived from fluorinated monomers (Figure 6). Rogers at DuPont in 1964 synthesized a CPI from 2,2-bis (3,4-dicarboxyphenyl)-hexafluoro propane dianhydride (6FDA) and 4,4'-(hexafluoroisopropylidene) dianiline (6FpDA). Later, Stclair (1985) and co-workers developed a series of CPIs based on 6FDA and diamines such as 4,4'-oxydianiline (ODA). Reuter *et al.* (1988), reported additional CPIs based on 6FDA combined with diamines such as ODA, 3,3'-6F, and 4,4'-6F for optical waveguide applications. Among the various fluorinated CPIs, the 6FDA/TFDB polyimide, synthesized from 2,2-bis (3,4-dicarboxyphenyl) hexafluoro propane dianhydride (6FDA) and 2,2-bis (trifluoromethyl)-4,4'-diaminobiphenyl (TFDB), is considered one of the most successful systems. This polyimide exhibits excellent optical transparency in the visible region, near-colorless characteristics, low dielectric constant, good solubility in polar organic solvents, and outstanding thermal stability, with a glass transition temperature (T_g) exceeding 300 °C (Matsuura *et al.*, 1991). Ando *et al.* (1992) developed perfluorinated polyimides that contain no hydrogen atoms, although these films were not completely colorless. Choi *et al.* (2009) synthesized highly colorless tetra-chlorinated polyimides from 2,2',5,5'-tetrachlorobenzidine (TCDB). Notably, the fully aromatic BPDA/TCDB polyimide demonstrated exceptional optical performance, with a $T_{400} \approx 82\%$. Xi *et al.* (2024) also synthesized four aromatic colorless polyimides (4,7-9) for optoelectronic applications.

Despite their outstanding optical and thermal properties, these aromatic CPIs face several limitations. Their synthesis is often complex and costly, making them less practical as substrate materials compared to other polymers. Additionally, their CTE values are relatively high, whereas electronic device applications typically require CTE values below 20 ppm/°C.

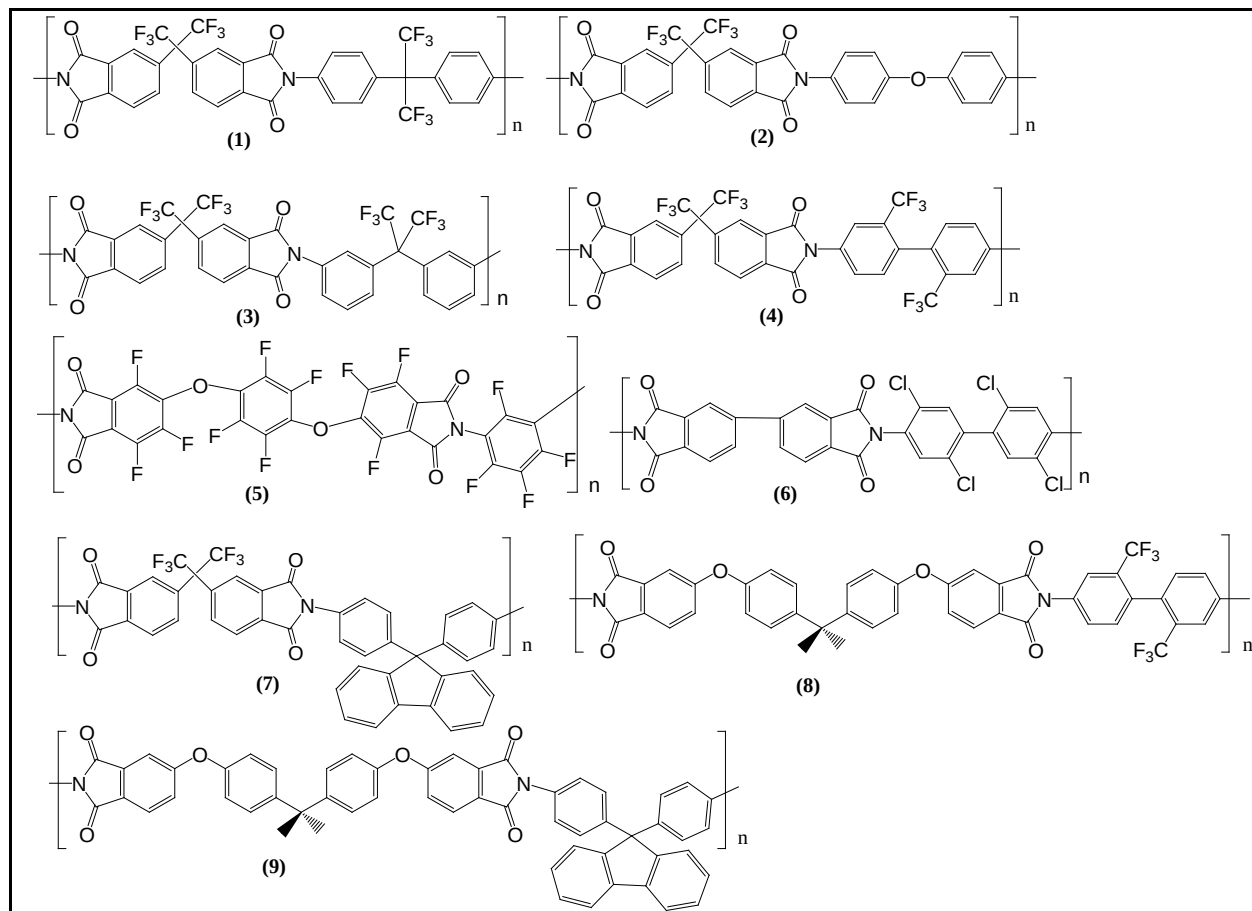


Figure 6: Aromatic Colorless PIs

A highly effective strategy for the synthesis of CPIs involves the incorporation of cycloaliphatic (non-aromatic) diamine and/or dianhydride monomers into the polymer backbone. Alicyclic polyimides have attracted considerable attention for optoelectronic and interlayer dielectric applications owing to their superior optical transparency and lower dielectric constants compared with fully aromatic polyimides. These favorable properties are primarily attributed to their lower molecular packing density, reduced chain polarity, and suppressed intra- and intermolecular charge-transfer (CT) interactions. However, significant challenges remain. The use of aliphatic diamines-in particular alicyclic diamines such as *trans*-1,4-cyclohexanediamine (t-CHDA) often results insoluble salts during the poly(amic acid) (PAA) formation step. This leads to premature chain termination or very low degrees of polymerization, ultimately yielding polymers with low molecular weight, which hinders their practical and industrial application.

In contrast, combining cycloaliphatic dianhydrides with aromatic diamine generally avoids salt formation and can produce colorless PIs. Nevertheless, many cycloaliphatic dianhydrides such as bicyclo [2.2.2] oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTA) exhibit poor reactivity toward aromatic diamines. This leads to low-molecular-weight PAAs and results in brittle PI films. In contrast, 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) stands out due to its unusually high reactivity, attributed to the ring strain in its anhydride structure. CBDA based PIs are usually colorless with high-molecular-weight, excellent thermal and mechanical properties. However, the inherently poor processability of these PIs significantly restricts their practical applications.

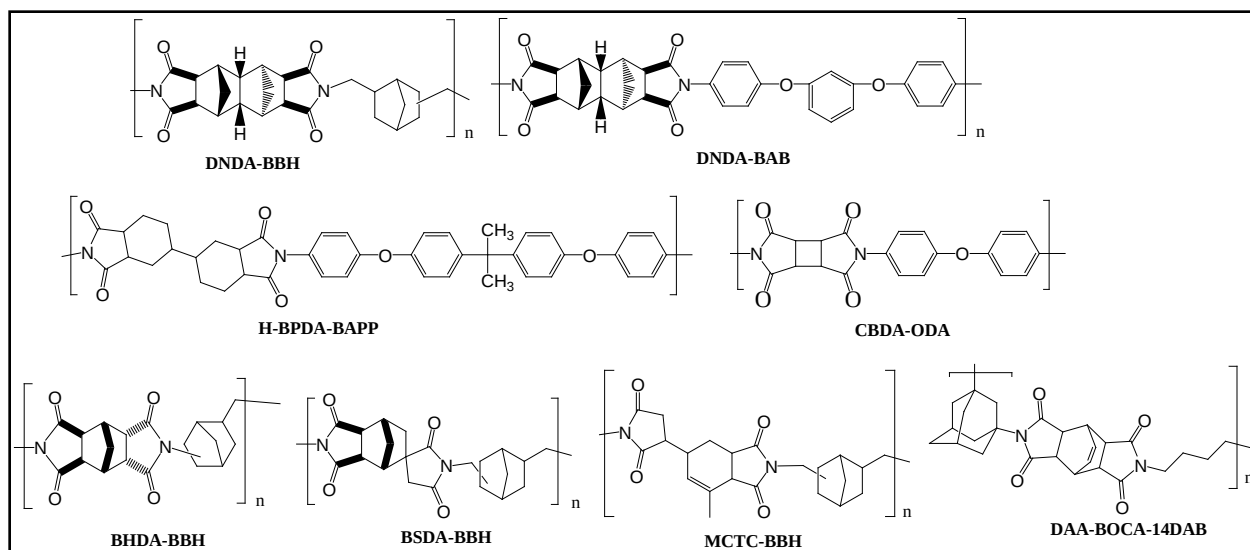


Figure 7: Non-aromatic Colorless PIs

Various alicyclic PIs have been developed to address these challenges. For instance, Matsumoto reported fully alicyclic PIs (DNDA-BBH, Figure 7) derived from polyalicyclic dianhydrides and bicyclic diamines, which exhibited exceptional glass transition temperatures (T_g) up to 400 °C while maintaining excellent colorlessness (Matsumoto, 1999). Similarly, systems based on dicyclohexyl tetracarboxylic dianhydrides combined with aromatic diamines (H-BPDA-BAPP) produced thermally stable (T_g between 210–270 °C) and transparent PI films (Shiotani *et al.*, 2001). Another cycloaliphatic dianhydride, CBDA is among the most effective monomers for producing colorless polyimides. Polyimides formed by combining CBDA with various aromatic diamines (e.g., 4,4'-oxydianiline and related structures) exhibit high transparency, good thermo-mechanical strength and low CTE, although their solubility remains limited when rigid diamines are used (Hasegawa *et al.*, 2007). Other cycloaliphatic dianhydrides, such as CPDA (Matsumoto, 2000) and hydrogenated pyromellitic dianhydrides (HPMDAs), have also been investigated. These exist in multiple isomeric forms with varying polymerizability and properties; for example, H'PMDA-based PIs tend to exhibit lower CTE due to greater chain linearity and rigidity (Hasegawa *et al.*, 2014). In addition, a wide variety of semi-aromatic and fully aliphatic PIs have been synthesized from different polyalicyclic dianhydrides and diamines [bis(2-hydroxyethyl) dodecylamine (BHDA), bis(sulfonamide) diamine (BSDA), Mast Cell Tryptase and Chymase (MCTC), Berberine Hydrochloride (BBH) in Figure 7 and 8]. These systems generally yield colorless, flexible, and free-standing films with good solution processability and high T_g values (typically 280–402 °C). Their optical properties include short cut-off wavelengths (below 235 nm for non-aromatic PIs and ~290–330 nm for semi-aromatic PIs), indicating excellent transparency.

A particularly effective structural motif is the incorporation of adamantane units—rigid, cage-like alicyclic structures—which enhance thermal stability without compromising transparency, solubility, dielectric properties, or CTE (Mathews *et al.*, 2006). Consequently, adamantane-containing semi-aromatic PIs have emerged as promising materials, combining high thermal resistance with desirable optical and processing characteristics.

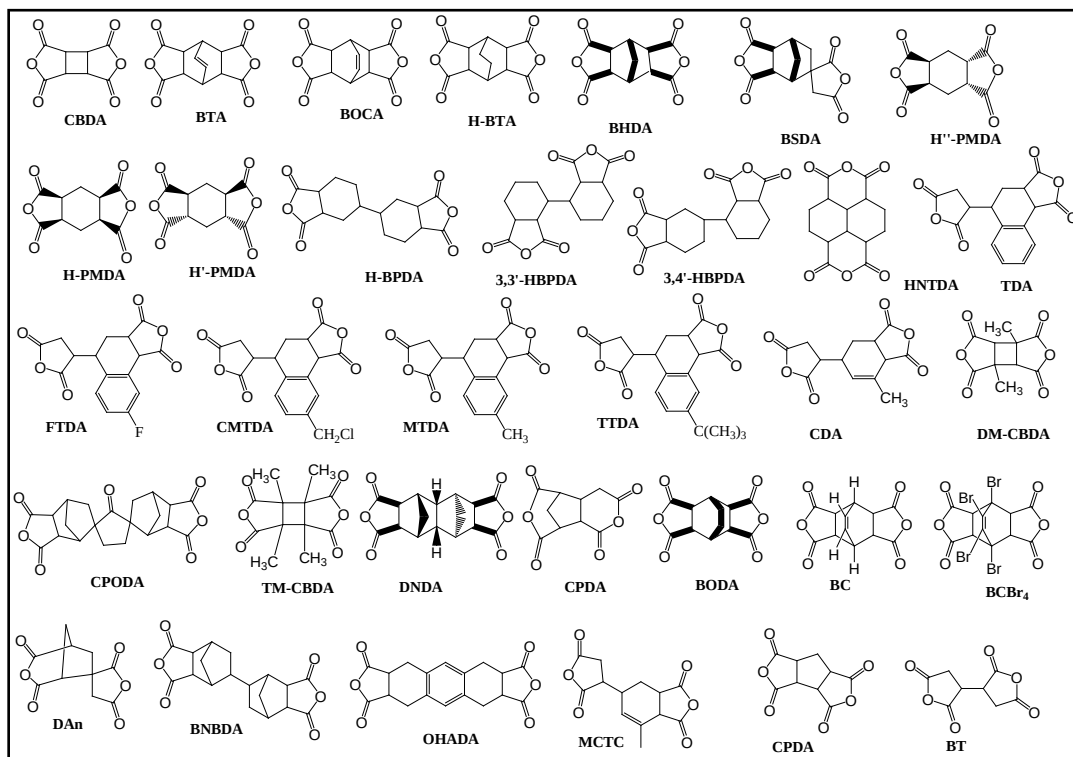


Figure 8: Cyclo-alicyclic Dianhydride Monomers

Non-aromatic (alicyclic) PIs generally exhibit excellent optical transparency along with satisfying solution processability and reasonable thermal stabilities. However, aliphatic polyimides are generally suitable only for applications requiring relatively low thermal stability. This is because the presence of aliphatic moieties increases chain flexibility and reduces backbone rigidity, leading to lower bond strength. Consequently, aliphatic polyimides generally exhibit lower thermal and dimensional stability than their fully aromatic counterparts.

Polymerization

Polyimides are typically synthesized via condensation polymerization of tetracarboxylic dianhydrides and diamines in dry, high-boiling polar solvents, such as Dimethyl Sulfoxide (DMSO), N,N-Dimethylformamide (DMF), N,N-Dimethylacetamide (DMAc), N-Methyl-2-pyrrolidone (NMP), gamma-butyrolactone (GBL), and *m*-cresol, to produce homogeneous poly(amic acid) (PAA) solutions. NMP is widely used for its strong solvency and relatively lower toxicity, but it can cause film coloration, often more than DMAc. GBL is a better alternative due to its balanced solubility, easier removal, lower hygroscopicity, and good oxidative stability. Molecular weight can be controlled by stoichiometric imbalance or monofunctional additives, while high monomer purity and contamination-free conditions are essential for achieving high optical transparency.

General two step synthesis

Polyimides (PIs) are mainly synthesized via a two-step polycondensation process (Figure 9). First, dianhydride and diamine react in polar aprotic solvents such as DMAc and NMP at low temperatures to form PAA. The PAA solution is then cast and imidized—either thermally (up to ~300°C) or chemically (e.g., using acetic anhydride/pyridine). Thermal imidization yields insoluble PIs with higher T_g and thermal stability due to greater molecular ordering, while chemical imidization produces more soluble and transparent PIs.

In chemical imidization, excess acetic anhydride (Ac_2O) and pyridine are added to the PAA solution, followed by stirring at room temperature for 12–24 h. This approach generally requires highly soluble polymer systems to prevent gelation or precipitation during the imidization process. The polymer is then precipitated, washed, and dried to obtain PI powder, with thorough removal of residual reagents to prevent side reactions and coloration. Chemically imidized PIs show better solubility, high optical transparency, and can be processed at lower temperatures ($\leq 250^\circ\text{C}$), mainly due to end-capping of reactive amino groups.

Highly basic diamines—especially aliphatic or alicyclic ones like *trans*-1,4-cyclohexanediamine (*t*-CHDA)—can form insoluble salts with dianhydrides during PAA formation, leading to poor polymerization and very low molecular weight ($\eta_{\text{inh}} \sim 0.07\text{--}0.08 \text{ dLg}^{-1}$). In contrast, cycloaliphatic dianhydrides with aromatic diamines avoid this issue and yield high-quality, colorless PIs. For polyalicyclic diamines, slow addition of diamine to the dianhydride solution is crucial to obtain a homogeneous PAA, while reversing the order often causes precipitation—an effect not seen with aromatic diamines.

One Step Synthesis

The one-pot thermal imidization procedure is well-suited for less reactive aromatic, fluorinated, and aliphatic/alicyclic monomers that often form insoluble salts during PAA formation. By conducting polycondensation at elevated temperatures without isolating PAA, this approach enables the synthesis of high-molecular-weight, soluble PIs. It is particularly effective for aliphatic polyimides, as imidization regenerates amines from salts, allowing polymerization to proceed. Typically carried out in solvents like *m*-cresol or DMAc with catalysts (e.g., isoquinoline), the process occurs at moderate temperatures ($160\text{--}200^\circ\text{C}$), minimizing side reactions. Overall, this method offers an efficient route to high-quality PIs when conventional two-step synthesis is limited by salt formation or low monomer reactivity.

Preparation of Polyimide Film in the Laboratory

The colorization of polyimide (PI) films is strongly affected by the preparation method. In the conventional PAA route, monomers are polymerized in solvents (e.g., DMAc, NMP), cast as films, and thermally imidized at high temperatures ($300\text{--}350^\circ\text{C}$).

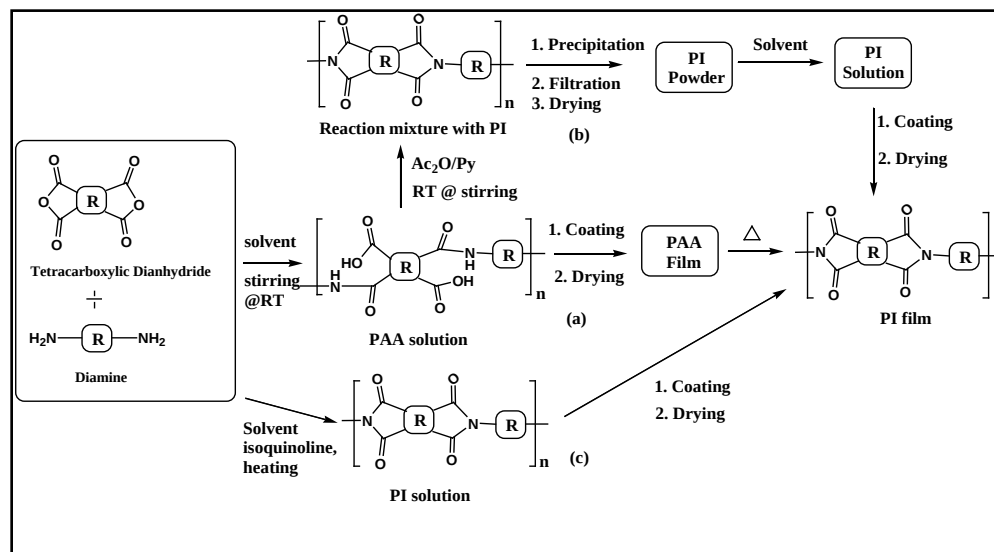


Figure 9: Synthesis and Film Fabrication of Polyimides Through Different Processing Routes: (a) Two-Step Thermal Imidization, (b) Chemical Imidization, and (c) One-Pot Method (Tapaswi & Ha, 2019)

However, instability of Peracetic acid (PAA) and high-temperature curing—especially in air—often lead to significant coloration, making this method less suitable for highly transparent films. In contrast, organo-

soluble PI solutions can be directly cast and dried at relatively lower temperatures ($\leq 250^{\circ}\text{C}$), avoiding high-temperature imidization and thus minimizing discoloration (Figure 9). Overall, reducing thermal exposure and preventing oxidative conditions are key to achieving colorless PI films.

Recent Molecular Design Strategies for the Development of Colorless Polyimides

A sufficiently high optical transmittance ($T_{400} > 80\%$) is essential for the application of PI films as substrates in display devices. To date, various molecular design strategies have been developed for the synthesis of CPIs. These include incorporating alicyclic structures, introducing bulky pendant groups (e.g., biphenyl, anthrone, fluorene and xanthenes), strong electron-withdrawing groups ($-\text{CF}_3$, $-\text{SO}_2-$), and using non-coplanar 2,2'-disubstituted biphenyl units, ortho-substituted diamines etc. These modifications help suppress charge-transfer interactions and improve optical transparency while preserving thermal performance. In this section, the most recent developments in the synthesis of colorless aromatic and non-aromatic PIs have been discussed in detail.

Introduction of Alicyclic Structures

Semi-alicyclic CPIs with improved dimensional stability were developed by Jiang and co-workers through the polymerization of amide-containing aromatic diamines, including 2,4-Diaminobutyric acid (Me DABA) and Chlorine-substituted diaminobenzanilide (CIDABA) (Figure 10), with alicyclic dianhydrides such as HPMDA and HBPDA (Figure 8) (Jiang *et al.*, 2020). The incorporation of rigid amide-linked diamine units effectively enhanced chain rigidity and suppressed thermal expansion behavior in the resulting PI films. Among the synthesized systems, the HPMDA–Me DABA-based CPI demonstrated the most favorable combination of thermo-mechanical and optical properties, exhibiting a low coefficient of thermal expansion (33.4 ppm/K, 50–250°C), a high glass transition temperature (349°C), and excellent thermal stability with a T5% value of 438.1°C. In addition, the film maintained high optical clarity, showing a transmittance of 82.3% at 400 nm for a thickness of 25 μm , together with low yellowness and haze values of 2.18 and 2.15%, respectively. These findings demonstrate that the introduction of rigid-rod amide functionalities into semi-alicyclic PI backbones is an effective molecular design strategy for achieving low-CTE CPI films with balanced thermal and optical performance suitable for optoelectronic substrate applications.

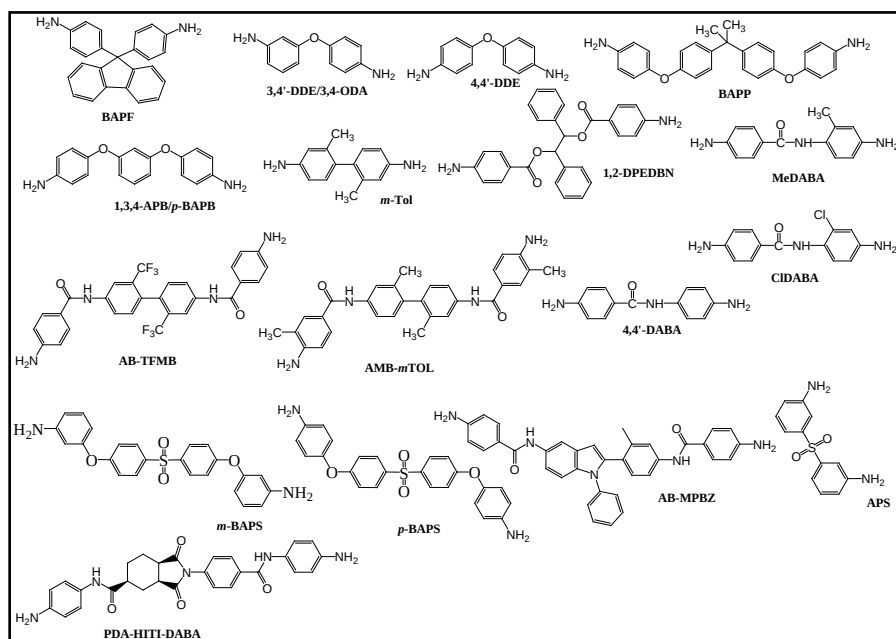


Figure 10: Aromatic Diamines Used for Semi-Aromatic CPIs Synthesis

Miao *et al.* (2020) successfully synthesized three novel adamantane-containing diamines-ADMDA, DMADMDA, and FADMDA (Figure 11) via Friedel–Crafts alkylation. Using these diamines along with four dianhydrides (6FDA, HPMDA, BPDA, and BTDA), three series of polyimides (PIs) were prepared through a one-step thermal imidization process. The results demonstrated that the incorporation of highly rigid, bulky, and non-coplanar adamantane moieties into the polymer backbone significantly improved the thermal, mechanical, and optical properties of the resulting polyimides, while simultaneously maintaining good solubility, unlike conventional aromatic polyimides. The T_g and 5% weight-loss temperature ($T_{5\%}$) values ranged from 285–440°C and 444–540°C, respectively, matching or surpassing those of traditional aromatic systems. In particular, CPIs derived from DMADMDA and alicyclic dianhydrides exhibited outstanding optical properties, including λ_0 below 300 nm, transmittance (T_{400}) above 80%, and low color intensity. The presence of two *ortho*-methyl substituents in DMADMDA increased interchain spacing (d-spacing), leading to higher T_g , lower CTE, and improved optical transparency. However, this modification resulted in somewhat reduced mechanical properties compared to ADMDA- and FADMDA-based counterparts.

Another cycloaliphatic dianhydride, CpODA (Figure 9), was polymerized with various aromatic diamines—1,3-BAB, 4,4'-DDE, 3,4'-DDE, 4,4'-DABA, and *m*-TOL—through both chemical and thermal imidization methods to produce semi-alicyclic polyimides (PIs) (Prof. Toshihiko Matsumoto group) (Ozawa *et al.*, 2021). Most of the PI films exhibited excellent thermal stability, with $T_{5\%}$ above 450°C, decomposition temperatures between 475 to 501°C and T_g exceeding 330°C. The films also demonstrated CTE in the range of 17–57 ppm/K. All prepared PI films were completely colorless, with cutoff wavelengths below 337 nm, indicating high optical transparency. Notably, the films synthesized via the chemical method displayed superior optical performance, which was attributed to an “end-capping effect.”

Hasegawa *et al.* (2022), synthesized amide/imide-containing aromatic diamines, including AMB-*m*TOL, AB-ATAB, AB-APAB, AB-TFMB, AB-*m*TOL, and PDA-HTI-DABA (Figure 10). The diamine was polymerized with H-PMDA in γ -butyrolactone (GBL). The polyimide films of H-PMDA/AB-TFMB and H-PMDA/AMB-*m*TOL exhibited a well-balanced set of properties, including low CTE in the range of 24–30 ppm/K, high optical transparency ($T_{400} > 80\%$), elevated glass transition temperatures ($T_g > 360^\circ\text{C}$), and adequate ductility.

Ingo Pinnau and co-workers reported the synthesis of two new organo-soluble and colorless polyimides via the polycondensation of two bicyclic alicyclic dianhydrides, BC and BCB $_4$, with the spirobisindane-based diamine SBIDA (Figure 11) (Abdulhamid *et al.*, 2019). The resulting CPIs exhibited good thermal stability, with decomposition temperatures of approximately 420°C and 352°C and also showed intrinsic microporosity. These polyimides were readily solution-processable and demonstrated strong mechanical performance, with tensile moduli in the range of 1.15–1.4 GPa, tensile strengths of 27–28 MPa, and elongation at break between 2% and 4%. Notably, the BCB $_4$ –SBIDA system displayed very high oxygen (O_2) permeability while maintaining comparable O_2/N_2 selectivity. These CPIs are considered promising candidates for membrane-based air separation applications owing to their favorable combination of optical transparency, solubility, and thermal stability.

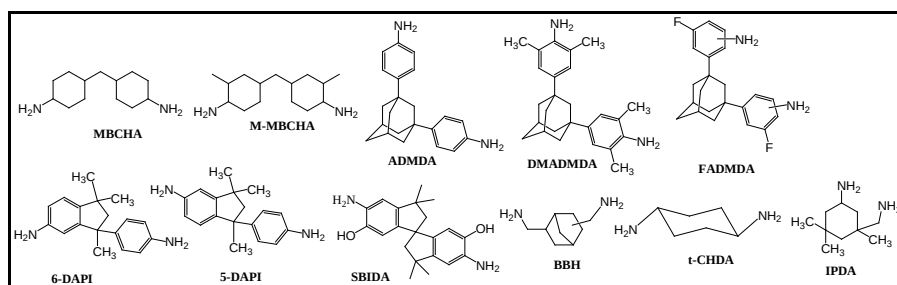


Figure 11: Cycloaliphatic Diamine Monomers Discussed in This Chapter

Hasegawa and co-workers carried out extensive investigations on the development of highly ductile colorless cycloaliphatic polyimide (PI) films, aiming to overcome the intrinsic brittleness commonly associated with such materials (Hasegawa, 2017). Their work systematically clarified the influence of molecular structure on the mechanical flexibility of cycloaliphatic PIs. In thermally imidized systems derived from 4,4'-ODA and various tetracarboxylic dianhydrides, the film ductility was found to decrease in the order of HQDA > PMDA > s-BPDA > TA-HQ > CBDA, indicating that CBDA-based systems are less favorable for achieving mechanically robust and flexible PI films.

The study further demonstrated that the incorporation of ether-linked dianhydrides, including BPADA, ODPDA, and HQDA, effectively enhanced the ductility of polyimides prepared from the rigid cycloaliphatic diamine t-CHDA, with BPADA (Figure 12) exhibiting the most significant toughening effect. In the case of the more flexible MBCHA-based system, copolymerization of PMDA/MBCHA with a small amount of IPDA (5–30 mol%) unexpectedly produced substantial improvements in film toughness, despite the inability of the corresponding PMDA/IPDA homopolyimide to form flexible films. In particular, the copolyimide containing 20 mol% IPDA displayed a remarkable elongation at break of 57%, together with high optical transparency ($T_{400} = 83.7\%$) and a high glass transition temperature ($T_g = 317^\circ\text{C}$). The enhanced ductility was attributed to increased chain mobility and facilitated intermolecular chain slippage within the polymer network.

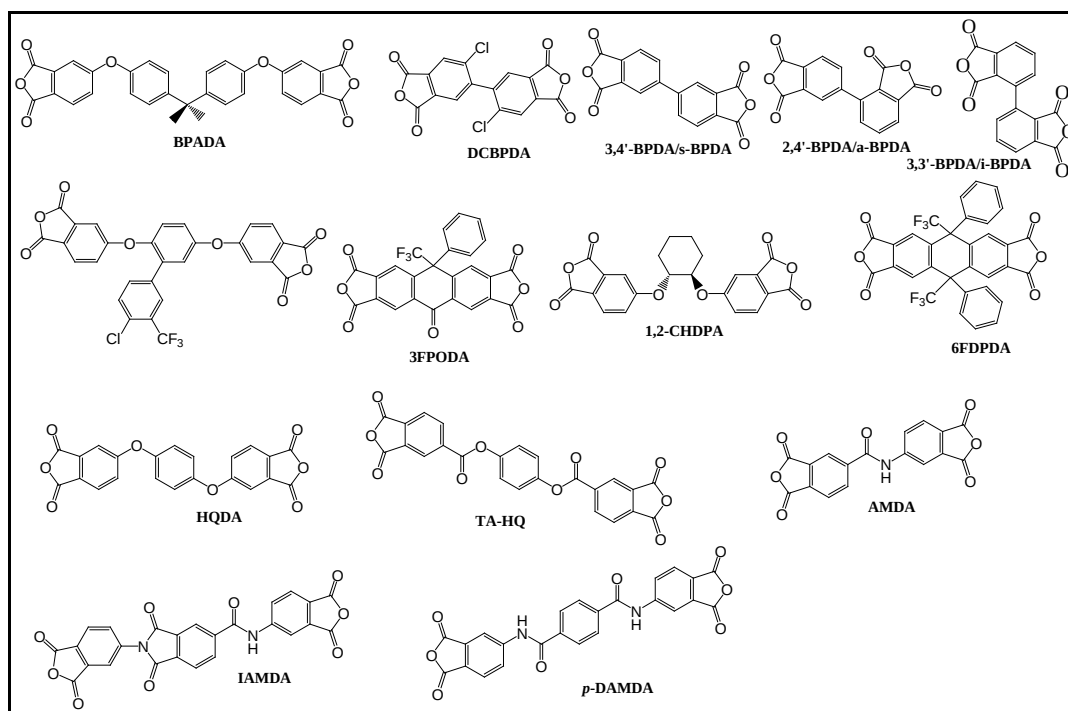


Figure 12: Dianhydride Monomers Discussed in This Section

A novel alicyclic dianhydride, OHADA, was synthesized and polycondensed with 4,4'-ODA to afford a colorless PI film exhibiting high thermal stability with $T_g > 300^\circ\text{C}$. This elevated T_g was attributed to the rigid OHADA structure lacking rotatable single bonds (Hasegawa *et al.*, 2023). Further polymerization with TFMB enhanced the thermal performance, yielding a PI with $T_g \approx 340^\circ\text{C}$ and improved decomposition resistance (higher T_d^5 under N_2) compared to other TFMB-based semi-alicyclic systems, although the CTE remained relatively high. The OHADA/TFMB system also exhibited pronounced thermoplastic behavior, likely due to its ladder-like, sterically distorted structure. Subsequent incorporation of AB-TFMB further

increased T_g to 355°C and reduced the CTE to 41.5 ppm/K, while preserving high optical transparency and good solubility.

Introduction of strong electronegative groups such as trifluoromethyl ($-\text{CF}_3$) or fluorine atoms in polyimide main chains

Fluorinated polyimides (PIs), particularly those incorporating trifluoromethyl ($-\text{CF}_3$) groups into their main chains, have been widely studied as an effective strategy to suppress charge-transfer complex (CTC) formation and thereby enhance optical transparency and solution processability without deteriorating their excellent properties. In general, increasing the fluorine content in PIs leads to improved transparency and reduced coloration. For example, PI films containing approximately 28% fluorine exhibit significantly enhanced optical properties, with λ_0 around 310 nm and transmittance at 500 nm (T_{500}) of about 94%. However, despite these advantages, highly fluorinated PI films face serious challenges when used as transparent substrates in device fabrication processes such as cleaning, peeling and etching. These films often show poor solvent resistance, leading to swelling or even structural damage upon exposure to solvents, which can compromise device performance. One practical approach to address this issue is to reduce the fluorine content in the PI structure. However, this typically results in a noticeable deterioration of optical properties. Furthermore, the high cost of fluorinated diamine and dianhydrides presents an additional limitation, restricting the widespread application of highly fluorinated PI films.

Min *et al.* (2020) reported solution-processable fluorinated CPIs synthesized via one-step polycondensation of 6FDA with either 6FDAM (Figure 13) or TFMB, yielding 6FDA-6FDAM-PI and 6FDA-TFMB-PI. The resulting films exhibited smooth morphology and suitable surface energy, enabling their use as gate insulators in organic transistors, where enhanced device performance was attributed to improved semiconductor ordering and fluorine-rich interfacial effects (Min *et al.*, 2020).

Liu *et al.* (2016) developed fluorinated poly (ether imide)s from a novel bis (ether dianhydride) TFCPPDA (Figure 13) and various aromatic diamines (PDA, ODA, APB, 6FAPB, and 9F-CI-APB (Figure 13)). The resulting poly (ether imide) films were nearly colorless exhibiting high transparency ($\%T_{450} \approx 76\text{--}88\%$), low cutoff wavelengths (<370 nm), excellent solubility, and balanced thermal–mechanical properties. Furthermore, their refractive indices could be precisely tuned through copolymerization, ranging from 1.6217 to 1.5523. The optical performance was attributed to reduced intermolecular interactions induced by $-\text{CF}_3$ and $-\text{Cl}$ substituents.

Another type of TFMB-based fluorinated CPI was reported by Jikang Liu and co-workers. In this study, two series of copolyimide films, namely 3F6FP/C-PI-x and 3F6FP/H-PI-x, were synthesized using different molar ratios of 6FDA and 3FPODA dianhydrides (Figure 13) via chemical and thermal imidization processes, respectively (Liu *et al.*, 2026). The resulting colorless copolyimide films exhibited significantly enhanced the thermo-mechanical properties. CPI films resulted from chemical imidization exhibited better optical, thermal, and mechanical performance compared to those obtained via thermal imidization, indicating that the former imidization process is more suitable for fabricating high-performance CPIs. Among the samples, the 3F6FP/C-PI-4 film—prepared by chemical imidization with a 3FPODA to 6FDA molar ratio of 4:6—showed the best overall performance. Its optical and other key properties met the requirements for applications in transparent FPCBs.

A novel semi-alicyclic dianhydride, 6FDPDA (Figure 13) was recently developed by Wang *et al.* (2023). Colorless polyimide films were synthesized by copolymerizing 6FDPDA with two other commercially available aromatic dianhydrides (BPDA and 6FDA) and one fluorinated diamine, TFDB following two-step chemical imidization procedure (Wang *et al.*, 2023). Owing to its ladder-like semi-alicyclic framework, along with bulky $-\text{CF}_3$ and phenyl substituents, 6FDPDA offers two key advantages: effective disruption of conjugation along the polymer backbone and suppression of intermolecular chain stacking. These structural features significantly improve the thermal stability and optical transparency of the resulting CPI films. In particular, when 6FDA was employed as the comonomer, the resulting CPI films exhibited outstanding

performance, including high optical transmittance ($\%T_{550} \approx 90\%$), a low YI of 2.45, a CTE of 16.5 ppm/K, and a T_g exceeding 450 °C. All these findings demonstrate that 6FDPDA is a highly promising monomer for the development of high-performance CPI materials, especially for optoelectronic applications such as flexible AMOLED display substrates.

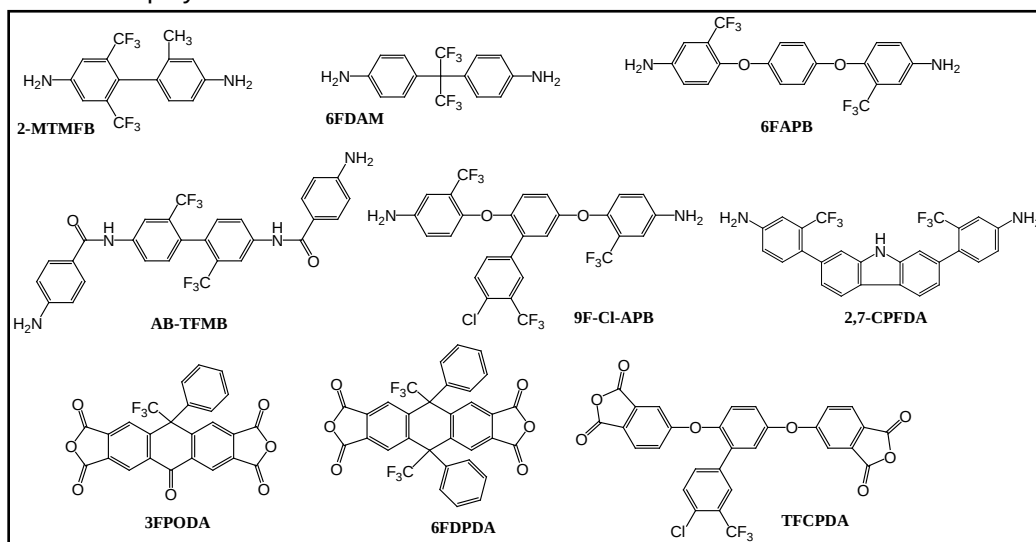


Figure 13: Trifluoromethyl (-CF₃) Substituted Monomers

Introduction of Bulky Pendant Substituents

The incorporation of bulky pendant groups such as biphenyl, anthrone, fluorene, and xanthenes into the polyimide network is widely regarded as an effective strategy to enhance solubility while retaining high thermal stability. These bulky substituents reduce chain conjugation and suppress intermolecular charge-transfer interactions, thereby minimizing coloration and improving optical transparency.

Wu *et al.* (2019b) synthesized a new diamine, Benzoporphyrin Derivative Monoacid ring A (BPDMA) (Figure 14), featuring bulky biphenyl pendant groups and *ortho*-dimethyl substitution, through a one-pot condensation reaction of 4-biphenyl carboxaldehyde and 2,6-dimethylaniline. Subsequently, BPDMA was polymerized with various dianhydrides through a one-step polycondensation process at elevated temperature. The resulting PI films were colorless to light yellow, with $\lambda_0 \approx 286\text{--}358$ nm and $\%T$ exceeding 80% in the 400–780 nm range. In addition, these PIs exhibited excellent solubility in common organic solvents, high T_g values (343–456°C), and good mechanical flexibility (Wu *et al.*, 2019 a).

A new diamine (BAPPA, Figure 14), incorporating anthrone units as pendant substituents was synthesized by Zhang *et al.* (2020). This monomer was polymerized with six different dianhydrides, including ODPA, to prepare polyesterimides with the aim of achieving a balanced combination of optical transparency and thermal stability. The incorporation of anthrone and pyridine moieties into the polymer backbone effectively restricted chain mobility, resulting in significantly enhanced thermal properties. The resulting polyesterimides exhibited high thermal stability with T_g values of 290–388°C. In addition, the cutoff wavelengths (λ_0) were between 374 nm to 427 nm, while the transmittance at 500 nm (T_{500}) was above 83% for films with a thickness of 40 μm . Notably, even the relatively flexible PIODPA-BAPPA system maintained a high T_g of up to 306°C, along with excellent optical transparency ($T_{500} = 89\%$) (Zhang *et al.*, 2020).

Hasegawa *et al.* (2019) synthesized symmetric and asymmetric spiro-type dianhydrides (TA-s-Spiro and TA-a-Spiro) and diamines (AB-s-Spiro and AB-a-Spiro) (Figure 14) containing ester linkages and fluorenyl pendant groups to prepare chemically imidized polyesterimides. The resulting polymers exhibited excellent solubility, high thermal stability, and good optical transparency due to the combined effect of ester linkages

and bulky fluorenyl moieties. Among them, the CBDA/AB-a-Spiro/TFMB-based polyesterimides showed an excellent balance of properties, including low CTE (10.5 ppm/K), high transparency ($T_{400} = 80.8\%$), and a high T_g of 351°C . The bulky, linear, and locally planar structure of AB-a-Spiro is believed to enhance solubility while simultaneously contributing to the reduced CTE in the resulting polyesterimides.

A new diamine, 9,9-Bis(4-aminophenyl)xanthene (BAPX) in (Figure 14), featuring a pendant xanthene unit, was synthesized and subsequently polymerized with various dianhydrides, including 6FDA. The incorporation of the xanthene unit was found to reduce the crystallinity of the resulting polymers, while significantly enhancing their optical transparency, solubility, and thermal performance. The obtained polyimide films exhibited λ_0 in the range of 367–415 nm, transmittance at 500 nm (T_{500}) between 73.2% and 84.1%, glass transition temperatures (T_g) of $308\text{--}348^\circ\text{C}$. Among them, polyimide derived from BAPX and 6FDA demonstrated the most balanced overall properties, with a λ_0 of 367 nm, T_{500} of 84.1% and T_g of 321°C (Zhang *et al.*, 2019).

Two aromatic diamines (24DABSBF and 35DABSBF) bearing spirobifluorene (SBF) units were synthesized via a four-step route involving bromination, borylation, Suzuki coupling, and subsequent reduction of dinitro intermediates. The resulting diamines were polymerized with PMDA, CBDA, and 6FDA through thermal or chemical imidization to yield six polyimides (PIs). The PI films, particularly PI-35CB, PI-356F, PI-24CB, and PI-246F, were nearly colorless and exhibited high optical transparency, with PI-35CB showing up to 95% transmittance at 400 nm. This excellent transparency was due to the amorphous nature induced by the bulky and rigid SBF units, which suppress intermolecular interactions and reduce chain packing. PIs derived from 35DABSBF showed slightly better transparency than those from 24DABSBF, likely due to the lower inherent coloration of the former monomer (Wen *et al.*, 2017).

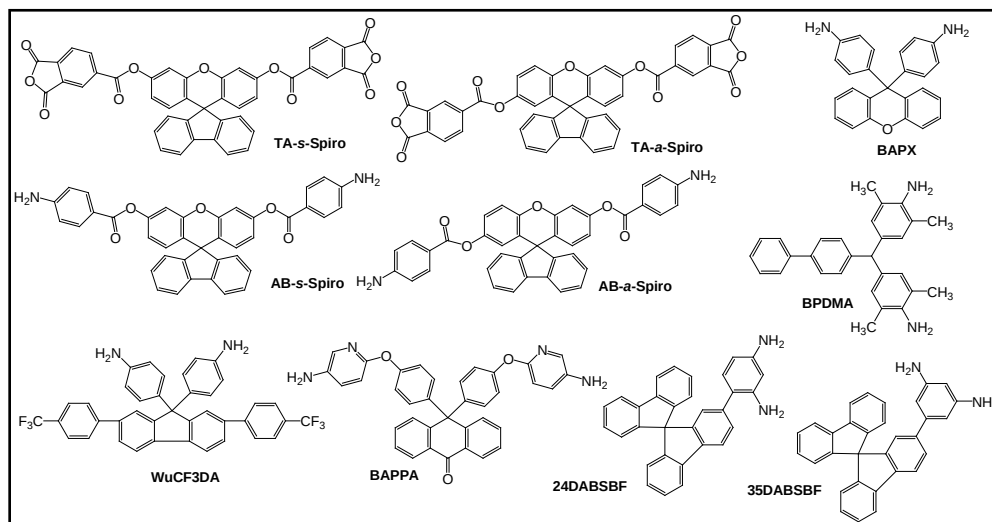


Figure 14: Diamines or Dianhydride Monomers with Bulky Pendant Substituents

Liu *et al.* (2017) synthesized a series of polyimides (PIs) incorporating bis(phenyl)fluorene units substituted with *p*-trifluoromethylphenyl groups. The diamine monomer (WuCF₃DA, Figure 14) features a non-planar structure, in which a conjugated fluorene core is connected to phenylamine units through a tetrahedral carbon, with $-\text{CF}_3$ groups at the terminal benzene rings. WuCF₃DA was prepared via bromination, Suzuki coupling, and subsequent reduction, with a high yield of 94%. WuCF₃DA-based PIs prepared from 6FDA, BPDA, BTDA, and PMDA exhibited excellent thermal stability (T_g up to 494°C), good solubility, and flexible amorphous films with nearly colorless appearance. The films showed cutoff wavelengths of 374–425 nm and high optical transparency, with WuCF₃-6FDA exhibiting 83.7% transmittance at 450 nm and over 90% in the visible region. The enhanced transparency was attributed to the disruption of conjugation by sp^3 -

hybridized fluorene carbons and the reduced intermolecular interactions caused by bulky aromatic side groups (Liu *et al.*, 2017).

Introduction of Substituents on The Ortho Position of Diamine

Substitution of methyl, isopropyl, or tert-butyl groups at the ortho position of aromatic diamines introduces steric hindrance around the imide C–N bond, thereby loosening chain packing and weakening intermolecular interactions. This effectively suppresses intermolecular charge-transfer complex formation, leading to enhanced optical transparency of PI films. Simultaneously, the restricted rotational mobility around the imide linkage increases chain rigidity and improves thermal stability, while the enlarged interchain spacing enhances polymer solubility.

Considerable attention has been devoted to the incorporation of methyl (Hasegawa *et al.*, 2022; Nam *et al.*, 2017; Bong *et al.*, 2016), isopropyl (Liu *et al.*, 2015) and tert-butyl (Yi *et al.*, 2015; Huang *et al.*, 2015) substituents at the ortho position of diamines to improve the performance of CPIs. Representative diamine containing these substituents are summarized in Figure 15. Liu *et al.* (2019) synthesized a series of semi-aromatic PIs using alicyclic dianhydrides (CHDA and BCDA) and methyl-substituted aromatic diamines containing bulky phenyl and fluorinated pendant groups, namely BAPM, BAFM, and BATFM (Figure 15). The resulting PI films exhibited excellent optical transparency with cutoff wavelengths of 282–286 nm and transmittance above 89% at 500 nm, along with high T_g values of 364–387 °C. In addition, the polymers showed low dielectric constants (2.72–2.80). Among them, the BATFM/CHDA-based PI demonstrated particularly outstanding transparency and minimal coloration despite its relatively low fluorine content (<10 wt%).

Wu *et al.* (2019b) reported several 6FDA based CPIs with aromatic diamines bearing methyl substituent (2255TMB, 33DMB and 22DMB, Figure 15) with varying number and positions via a one-step polymerization reaction. The resulting PIs showed good solubility, high thermal stability, low dielectric constants and appreciable optical transparency. Among them, 2255TMB-PI, containing four methyl substituents at the 2,2',5,5'-positions, showed the best overall performance, including high transparency ($T_{400} > 82\%$), high T_g (~407°C), excellent thermal stability ($T_{d5} > 500^\circ\text{C}$), low CTE (~34.3 ppm/K), and a low dielectric constant (~2.84). The enhanced properties were mainly attributed to the strong steric hindrance effect of the ortho-methyl groups.

Li and co-workers (2017) synthesized several soluble, optically transparent PIs with excellent thermal stability by using alkyl substituted diamine containing naphthalene units. Three naphthalene-based diamines bearing –H (BAN-1), –CH₃ (BAN-2), and –CH(CH₃)₂ (BAN-3) at the ortho-positions were synthesized and polymerized with ODPA, BPDA, and 6FDA via a one-step microwave-assisted method. All resulting PIs exhibited high optical transparency, with BAN-2 and BAN-3 based PIs showing cutoff wavelengths below 400 nm and transmittance exceeding 84% at 450 nm. Transparency increased with steric hindrance in the order: BAN-3 > BAN-2 > BAN-1, confirming the effectiveness of ortho-substitution in suppressing charge-transfer interactions. Thermally, BAN-2 based PIs showed the highest T_g (>340 °C), while BAN-3 based PIs exhibited relatively lower T_g values. These results demonstrate that increasing steric hindrance improves optical transparency but may slightly reduce chain rigidity and thermal performance.

Wu and co-workers (2020) synthesized a new semi-aliphatic diamine, CHMBTBA (Figure 15), containing bulky cyclohexyl and *ortho-tert*-butyl groups, and polymerized it with various aromatic dianhydrides to prepare semi-aliphatic PIs. The resulting films exhibited excellent solubility, high optical transparency (>86% in the visible region), low coloration, and high T_g values (>310°C). In addition, the polymers showed low water absorption and good mechanical properties. The study demonstrated that the incorporation of *tert*-butyl and cyclohexyl groups is an effective strategy for improving the transparency of PIs while maintaining excellent thermal performance.

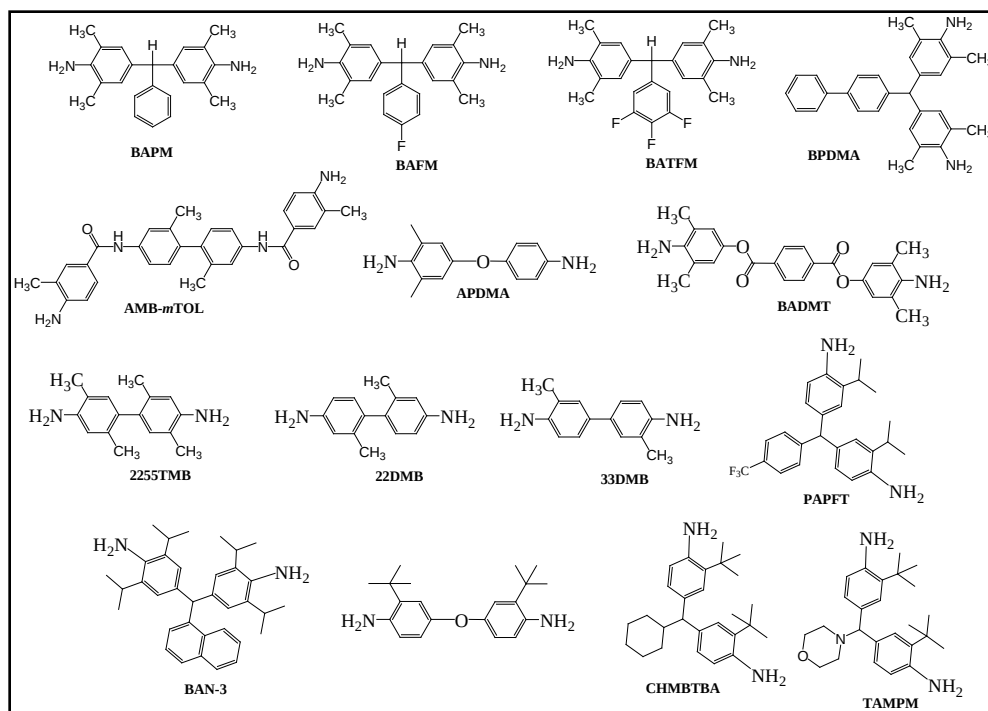


Figure 15: Ortho-Substituted Aromatic Diamines

Conclusion

Colorless and transparent polymeric materials possessing high glass transition temperatures (T_g), low coefficients of thermal expansion (CTE), and excellent thermo-mechanical performance are highly desirable for advanced optoelectronic applications. Among high-performance polymers, polyimides (PIs) are regarded as one of the few materials capable of maintaining T_g values above 300°C. Nevertheless, conventional fully aromatic PIs generally exhibit intense coloration, which restricts their application in optical and electronic devices requiring high transparency. This coloration primarily originates from intra- and intermolecular charge-transfer (CT) interactions between electron-donating diamine moieties and electron-accepting dianhydride units.

Considerable efforts have therefore been devoted to suppressing CT interactions through molecular design strategies, including the incorporation of bulky substituents, asymmetric or non-coplanar structures, fluorinated groups, and alicyclic segments. These modifications effectively enhance optical transparency and solubility while often preserving the excellent thermal properties of PIs. However, the practical development of colorless polyimides (CPIs) is still constrained by the high cost of fluorinated monomers and the relatively low reactivity and thermal stability associated with alicyclic monomers. Despite these challenges, CPIs are considered promising candidates for next-generation flexible and transparent electronic devices. Further research is needed to achieve a balanced combination of processability, optical transparency, thermal resistance, dimensional stability, and low CTE. In this regard, the development of novel monomer architectures through advanced synthetic methodologies, such as cross-coupling and multicomponent reactions, is expected to play a key role in improving performance while reducing production costs, thereby broadening the application potential of CPI materials.

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