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Chapter

# Design, Fabrication, and Application of Colorless Polyimide Film for Transparent and Flexible Electronics

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## Abstract

Driven by the emerging development of transparent and flexible electronics, colorless polyimide (CPI) has been attracting much attention in recent years. As a key component for next generation electronics, CPI film will be well focused both on research and commercialization. In this chapter, we would like to provide a review and outlook to the field for the reference of scientists, engineers, and entrepreneurs. Topics being addressed are formulation/design, synthesis of the resin, fabrication, and characterization of the CPI films, as well as trends of the film application for the next generation of electronics. Attention will also be given to the current stage of manufacturing of CPI monomers and resin, industrial production of CPI films, etc.

**Keywords:** colorless polyimide, design, fabrication, electronics

## 1. Introduction

Polyimides (PIs) are one of the most important classes of polymers with high mechanical properties, thermal stability, high temperature resistance, good chemical resistance, and dielectric features [1, 2]. Since their mass production in 1955 [3], they enjoy a superior role in the application of electronics, aerospace, automobile, and military fields for their excellent combined properties under harsh environment [4, 5]. With the rapid development of electronic industry, PI film has even become indispensable in microelectronic and optoelectronic engineering due to their high demand of lightweight, durable, and reliable materials [6]. PI films are used in image display devices, optical films, organic photovoltaics, flexible printing circuit boards, and other optoelectronic devices [7]. However, conventional colored PI films which have lower optical transmittance can't fulfill the need of optical transparency in electronic devices, and a reliable colorless polyimide (CPI) is highly desired.

The lower optical transmittance of conventional PI is caused by the formation of intra- and intermolecular charge transfer complex (CTC) originated from their conjugated structures [8, 9]. Therefore, the basic principle to increase the transparency of CPI is to avoid or reduce the conjugated units and suppress the CTC. To achieve this, two manners of molecular design are adopted in most of the CPI studies. One is to choose diamines with lower electron-donating capability or dianhydrides with lower electron-accepting capability to decrease the CTC induced by them [9]. For example, 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFMB) [10], which is used widely as the monomer of CPI material, has weaker electron-donating property than many diamines like p-phenylenediamine (PPD), 4,4′-oxydianiline (ODA) and will show lighter color if copolymerizing with the same dianhydride [9]. The similar phenomenon will happen to 3,3′,4,4′-biphenyl tetracarboxylic diandhydride (BPDA) with weaker electron-accepting property compared with pyromellitic dianhydride (PMDA) [9]. The other manner is to break the chemical regularity of the copolymer, like inducing the alicyclic structural unit [11, 12]. But in most cases, these two manners are combined together to improve the transparency of CPI. To be concrete, many CPIs are synthesized by introducing fluorine atoms, cyclic side groups, bulky substituents, flexible linkages, and so on [13–18].

Besides the monomers, the film preparation method can also influence the color of PI films by heat or solvents [15]. There are two conventional ways to prepare CPI films: PAA route and organo-soluble PI route. As heat treatment in air will cause coloration, it is suggested that the film preparation should be under inert gas atmosphere or in vacuum by PAA route, however, the high temperature about 300–350°C will still affect the transparency. If the CPIs are soluble, the solvent method will be a better way to prepare CPI compared to PAA route. But, it needs to be concerned that organo-soluble PIs may have relatively low heat and solvent resistance.

Since the discovery of CPI, quantities of studies have been done. In terms of patent layout, patent applications in the CPI field began in the 1970s and reached a peak in 2011. Among them, the number of patent applications in Japan ranks first, accounting for nearly half of the total number of applications.

After more than 30 years of development, the industrial production of CPI has been realized in recent years. While PI production has high technical barriers, there are only several main suppliers, including DuPont, Kaneka, Ube Industries, South Korea SKC, and Taimide, which occupy more than 90% of the global market. The number of CPI suppliers is even less, such as Kolon Industry, SKC, and Sumitomo Chemical. Sumitomo Chemical took up more than 95% of the global CPI films market in 2018. The main suppliers of CPI and their products are listed in **Table 1** [19].

Although CPI has been used in applications, like OLED and photovoltaics, there are still many aspects to be improved. For designing molecular structure, high-temperature stability, optical transparency, and other properties need to be balanced, as in many cases these properties contradict with each other. For PI film production, the major challenge is the high level of technical capabilities is needed to improve the yield. Other properties like water and gas properties need to be enhanced too.

| Company | Product name | Transmission | $T_g$ (°C) |
|---|---|---|---|
| MitsubishiGas Chemical | Neopulim® | 89–90 | 300–489 |
| DuPont-Toray | Colorless Kapton® | 87 | >300 |
| Kolon Industry | — | >89 | 330–350 |
| SKC | — | 89 | — |
| Sumitomo Chemical | — | >90 | — |
| HiPolyking | — | >90 | >330 |

**Table 1.**
*The main suppliers of CPI and their products.*

## 2. The formulation of CPI

Conventional aromatic PIs showing deep color by absorbing visible light intensely is not applicable in microelectronic and optoelectronic engineering. This is well known due to the formation of charge transfer complexes (CTCs) from the interactions between electron-donating diamine and electron-accepting dianhydride. Recent development shows that the suppression of CTC can be achieved by incorporating structures such as fluorinated group, alicyclic monomers, noncoplanar structure, meta-substitute structure, or sulpone into the main chain of PIs thus increasing the transparency of PI films [20]. According to the composition of main chain, colorless polyimides (CPIs) will be classified into fluorinated CPIs, alicyclic CPIs, noncoplanar CPIs, and other CPIs. The key monomers are listed below in tables to show the studies clearly (**Tables 2–6**).

### 2.1 Fluorinated CPIs

Examples of aromatic CPIs are largely dominated by fluorinated ones, as incorporating the charge negative fluorine atoms into the electron-donating diamine will suppress the formation of CTC and therefore increase the transparency of PI films. Furthermore, due to the larger volume of fluorine atoms, the free volume between the molecules are also increased which improves the dielectric properties of PIs. Despite the improvement of both optical and dielectric properties, the incorporation of fluorine atoms might lead to the lowering of mechanical strength and glass transition temperature ($T_g$).

### 2.2 Alicyclic CPIs

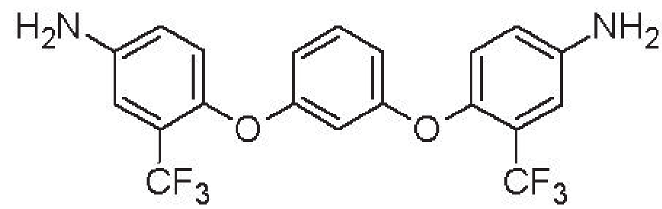
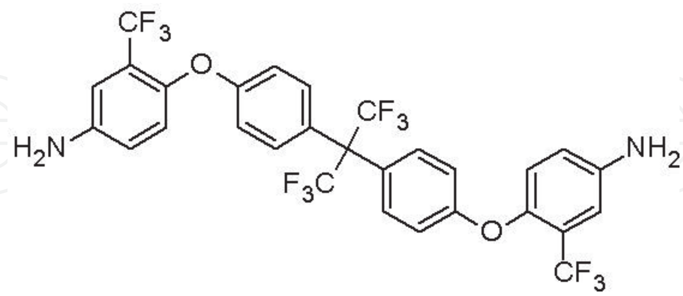
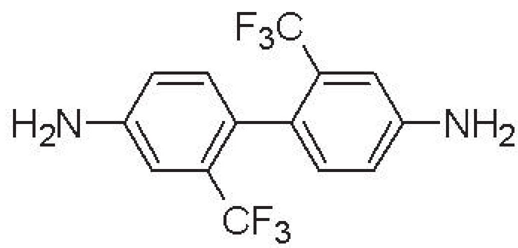
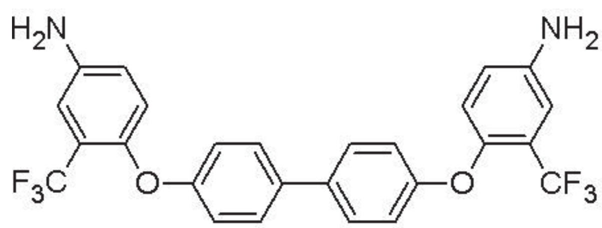
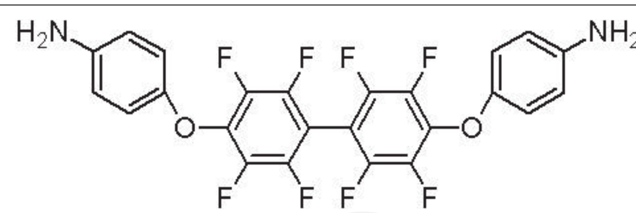
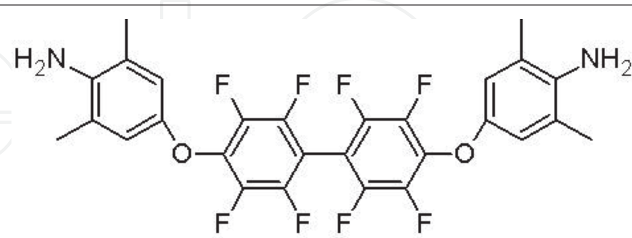
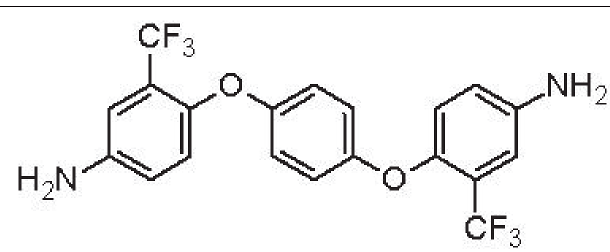
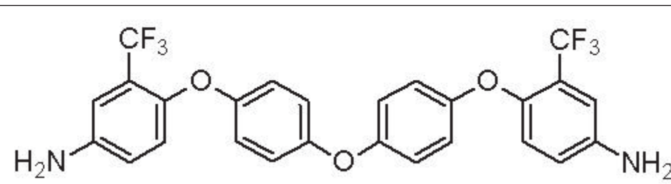
A more effective approach to synthesize CPIs is to use nonaromatic monomers either in diamines or dianhydrides. An alicyclic compound is an organic compound that contains one or more all-carbon rings, which may be either saturated or unsaturated but do not have aromatic character. By adopting the alicyclic moieties in the main chain of PI, the probability of undergoing inter- or intramolecular charge transfer (CT) is lower, which leads to an improvement in the optical properties of PIs. However, the incorporation of alicyclic unit generally reduces thermal stability and mechanical strength and both are crucial factors for PI. Therefore, it's important to consider the proportion of alicyclic structure without too much compromise on the thermal and mechanical properties.

### 2.3 Noncoplanar colorless PIs

Incorporation of noncoplanar structures into polymer chains is considered as one of the effective ways to improve the optical transparency of PIs without too much compromise of their thermal stability and mechanical strength. The nonplanar structure reduces the strong interaction and tight stacking of the molecular chains preventing the forming of CTC.

### 2.4 Other colorless PIs

Besides the monomers listed, there are also other structures that can be introduced into the PIs to improve the optical transparency of PI films. For instance, sulfonyl-substituted PIs exhibit good combined quality, including good thermal stability and high optical transparency within the visible light region. This is due to

| Monomer | Chemical structure | Ref. |
|---|---|---|
| 1,3-Bis(4-amino-2-trifluoromethyl-phenoxy)benzene |  | [21] |
| 2,2-Bis[4-(2-trifluoro-methyl-4-aminophenoxy)phenyl]hexafluoropropane |  | [22] |
| 2,2′-Bis(trifluoromethyl)-4,4′-diaminobiphenyl (TFMB) |  | [23, 24] |
| 4,4′-Bis(4-amino-2-trifluoromethylphenoxy)biphenyl |  | [25] |
| 4,4′-((Perfluoro-[1,1′-biphenyl]-4,4′-diyl)bis(oxy))dianiline |  | [26] |
| 4,4′-((Perfluoro-[1,1′-biphenyl]-4,4′-diyl)bis(oxy))bis(2,6-dimethylaniline) |  | [26] |
| 1,4-Bis(4-amino-2-trifluoromethylphenoxy)benzene |  | [25] |
| 4,4′-Bis(4-amino-2-trifluoromethylphenoxy)diphenyl ether |  | [27] |

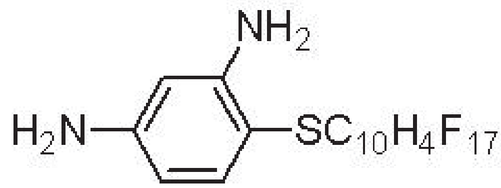
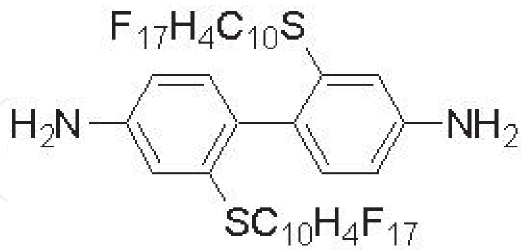
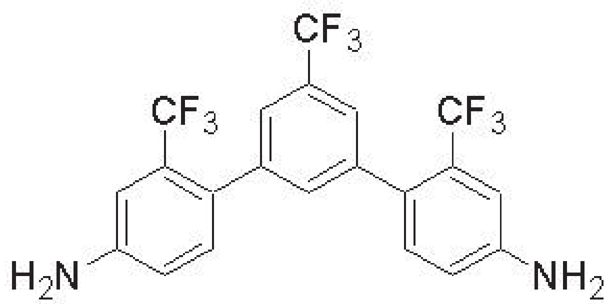
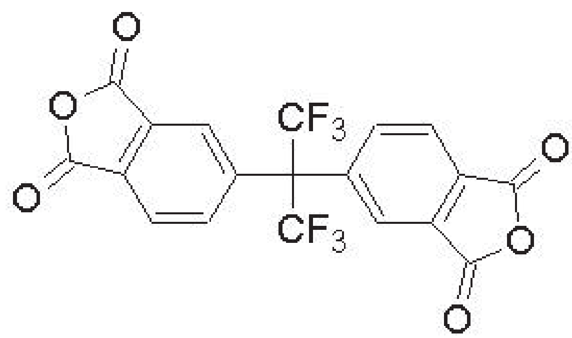
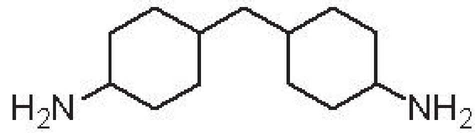
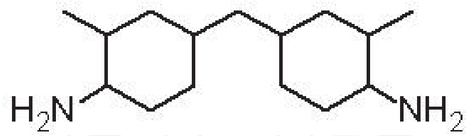
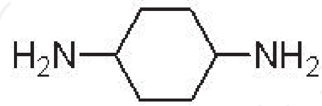
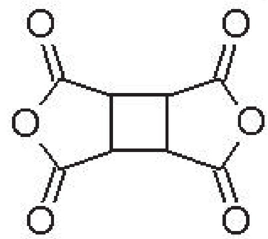
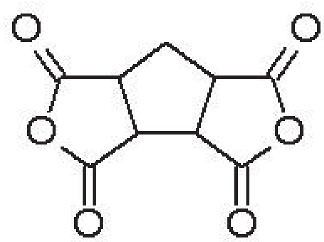
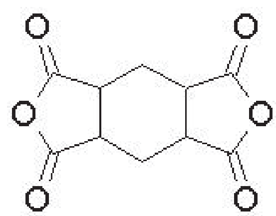
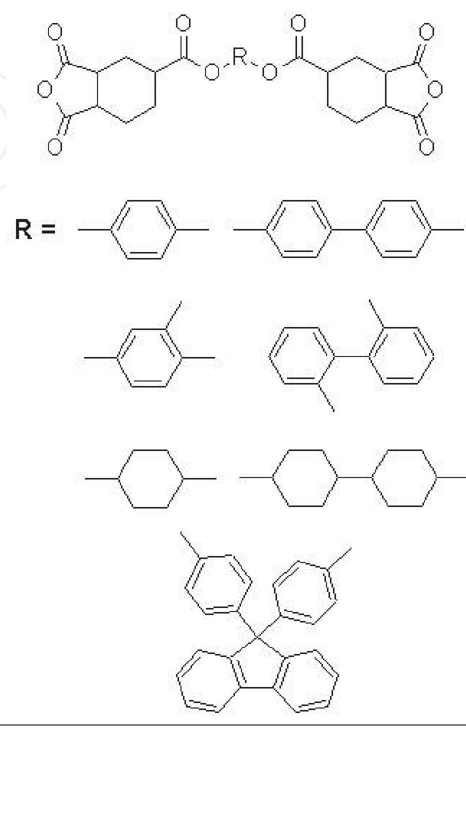
| Monomer | Chemical structure | Ref. |
|---|---|---|
| 2,4-Diamino-1-(1H,1H,2H,2H-perfluorodecathio) benzene |  | [28] |
| 2,2′-Bis((1H,1H,2H,2H-perfluorodecyl)thio)[1,1’-biphenyl]4,4′-diamine |  | [28] |
| 3,5-Di(2-trifluoromethyl-4-amino)-1-trifluoromethyl-tuluene |  | [29] |
| 2,2-Bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) |  | [23, 27, 28, 30–32] |

**Table 2.**
*Key monomers for fluorinated CPIs.*

the existence of charge-accepting sulfur atoms in sulfonyl suppressing the formation of CTC. Another example is incorporating meta-substituted diamine to increase the free volume which lowers the interaction between molecules and effectively reduces the CTC. Moreover, hyperbranched polymer is considered to have low probability of forming CTC due to their asymmetrical spherical loose structures with defect (**Table 6**).

## 3. CPI film production

In general, polymer film manufacturing techniques include several types, such as melting extrusion, casting, and blowing. There are many factors that affect the choice of polymer film production process, including physical and chemical properties, color and appearance requirements of polymer resins, and the existing capabilities of film production equipment. For crystalline polymer resins with clear melting points, such as PET and PEN, non-solvent melt extrusion technology is mainly used. For amorphous polymers with low to medium melting points, such as

| Monomer | Chemical structure | Ref. |
|---|---|---|
| 4,4′-Methylenebis (cyclohexylamine) (MBCHA) |  | [11] |
| 4,4′-Methylenebis(2-methylcyclohexylamine) |  | [33] |
| 1,4-Cyclohexanediamine (CHDA) |  | [11] |
| Cyclobutane tetracarboxylic dianhydride (CBDA) |  | [12, 25, 34] |
| Cyclopentane tetracarboxylic dianhydride (CPTA) |  | [25] |
| 1,2,4,5-Cyclohexanetetracarboxylic dianhydride |  | [25, 35] |
| Cyclohexanetricarboxylic–based dianhydrides |  | [11] |

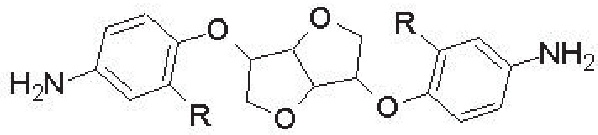
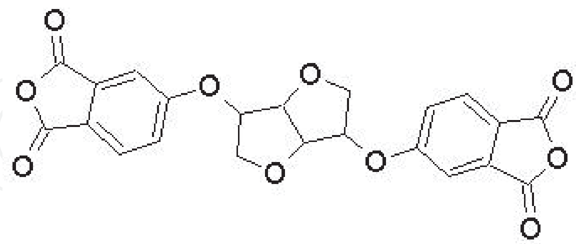
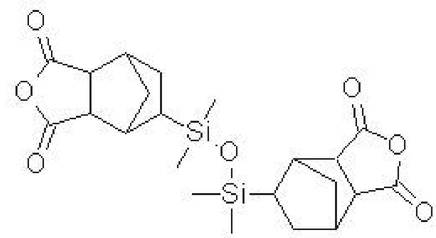
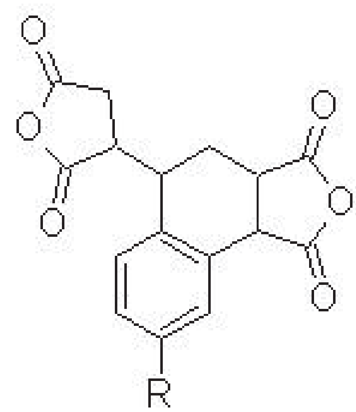
| Monomer | Chemical structure | Ref. |
|---|---|---|
| 1,4:3,6-Dianhydro-2,5-di-O-(4-aminophenyl)-D-mannitol |  R = H, $CF_3$ | [36] |
| 1,4:3,6-Dianhydro-2,5-di-O-(3,4-dicarboxyphenyl)-D-mannitol dianhydride |  | [36] |
| 5,5′-(1,1,3,3-Tetramethyl-1,3-disiloxanediyl) bisnorbornane-2,3-dicarboxylic anhydride |  | [27] |
| 3,4-Dicarboxy-1,2,3,4-tetrahydro-1-naphthalene succinic dianhydride (TDA) |  R = F, $CH_3$ | [37, 38] |

**Table 3.**
*Key monomers for Alicyclic CPIs.*



PC and PES, melt extrusion and solution casting are used. As PIs are amorphous polymers with high melting points due to their hard molecular skeleton, the solvent casting process [47] (as shown in **Figure 1**) is usually the best choice, especially in the laboratory.

The solvent casting process to prepare colorless polyimide film in the laboratory can be realized by two conventional film-forming routes, PAA and organo-soluble PI route [48–54]. Similar to the preparation of ordinary PI film, the PAA method to produce CPI just needs to add salivation, drying, stretching, and other steps in the middle of the two steps of PI polymer production, synthesis of polyamide acid, and imidization. In detail, the monomers of dianhydride and diamine are first polymerized in DMAc or NMP to form a PAA solution. A PAA film is then formed by casting the solution on a clean substrate. Finally, an imidization treatment is performed to produce a colorless PI film. Because PAA membranes are prone to

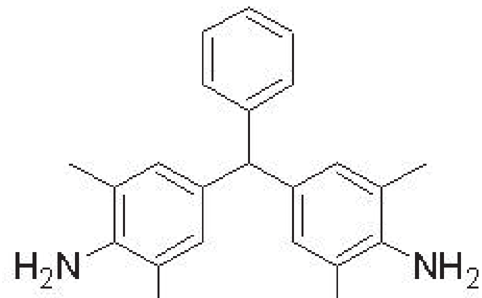
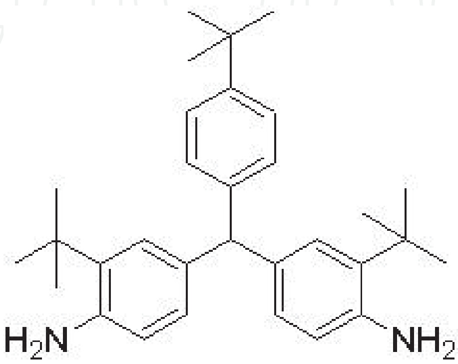
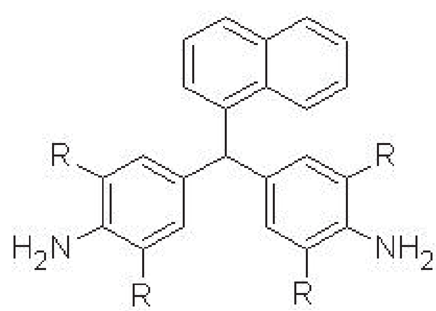
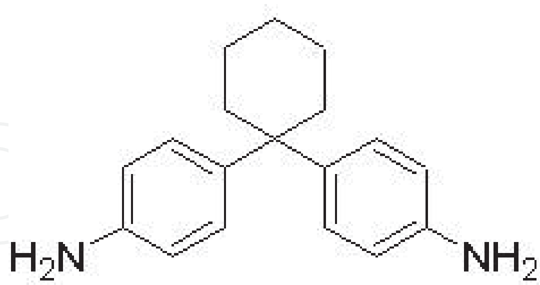
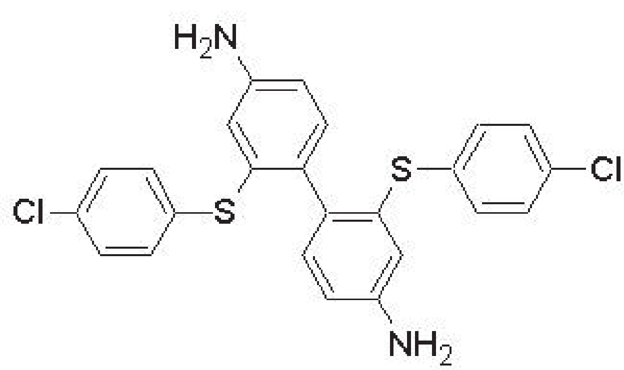
| Monomer | Chemical structure | Ref. |
|---|---|---|
| 3,3′,5,5′-Tetramethyl-4,4′-diaminodiphenyl-butyltoluene (BADP) |   | [39] |
| 3,3′-Ditertbutyl-4,4′-diaminodiphenyl-4″-tertbutylphenylmethane |   | [40] |
| 4,4′-(Naphthalen-1-ylmethylene)dianiline |   R = H, $CH_3$, $CH(CH_3)_2$ | [30] |
| 4-[1-(4-Aminophenyl) cyclohexyl]aniline |   | [24] |
| 2,2′-Bis(4-chlorothiophenyl) benzidine |   | [41] |

**Table 4.**
*Key monomers with large substituent group or side group.*

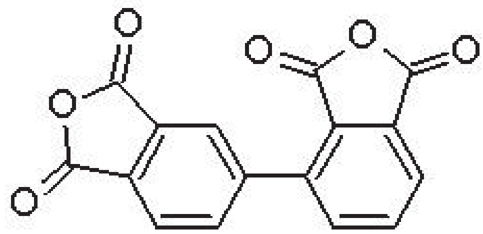
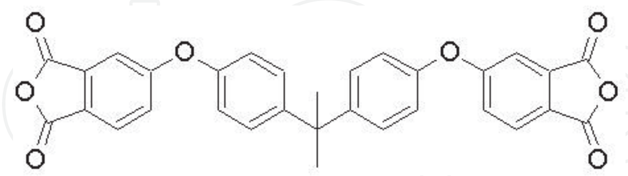
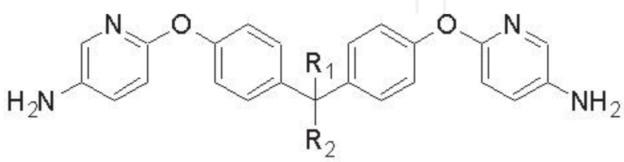
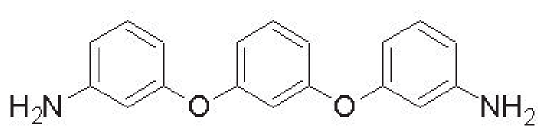
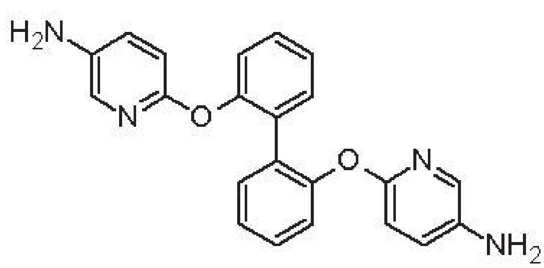
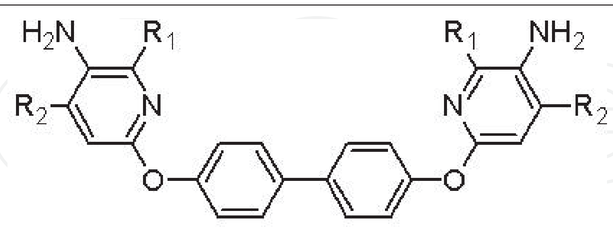
| Monomer | Chemical structure | Ref. |
|---|---|---|
| 2,3,3′,4’-Biphenyl tetracarboxylic dianhydride (a-BPDA) |  | [25] |
| 4,4′-(4,4′-Isopropylidenediphenoxy)bis (phthalicanhydride) (BPADA) |  | [17, 42] |
| 2,2′-Bis[4-(5-amino-2-pyridinoxy)phenyl]-propane |  $R_1 = R_2 = CH_3$<br>$R_1 = R_2 =$ phenyl<br>$R_1 = CH_3$, $R_2 =$ phenyl | [43] |
| 1,3-Bis(3-aminophenoxy) benzene |  | [42] |
| 2,2′-Bis(5-amino-2-pyridinoxy)biphenyl |  | [31] |
| 4,4′-Bis(5-amino-2-pyridinoxy)biphenyl |  $R_1 = H$, $R_2 = CH_3$<br>$R_1 = CH_3$, $R_2 = H$ | [31] |

**Table 5.**
*Key monomers in bended main chain of CPIs.*

thermal decomposition or hydrolysis, freshly synthesized PAA is usually used to prepare PI films. High-temperature curing can cause obvious coloring, so the preparation of CPI film should be carried out under vacuum or inert atmosphere. The curing process includes both solvent evaporation and dehydration imidization. In

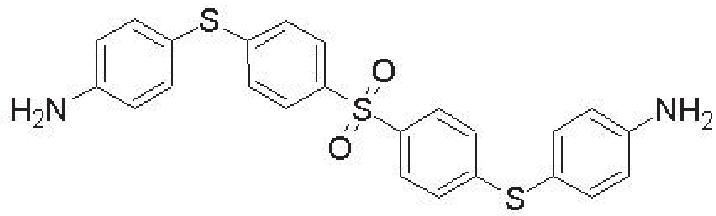
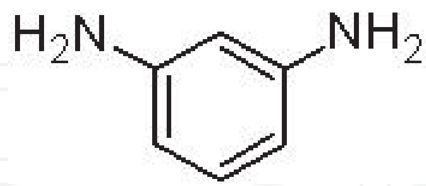
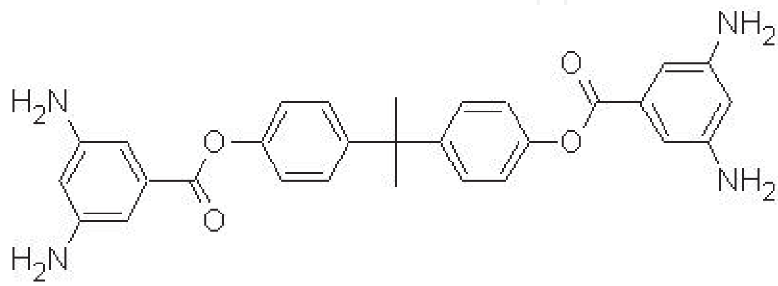
| Monomer | Chemical structure | Ref. |
|---|---|---|
| 4,4-Bis(4-amino-phenylenesulfanyl)diphenylsulfone |  | [44] |
| m-Phenylenediamine |  | [45] |
| Bisphenol A bis (3,5-diaminobenzoate) |  | [46] |

**Table 6.**
*Sulfonyl-substituted, meta-substituted, and hyperbranched monomers.*

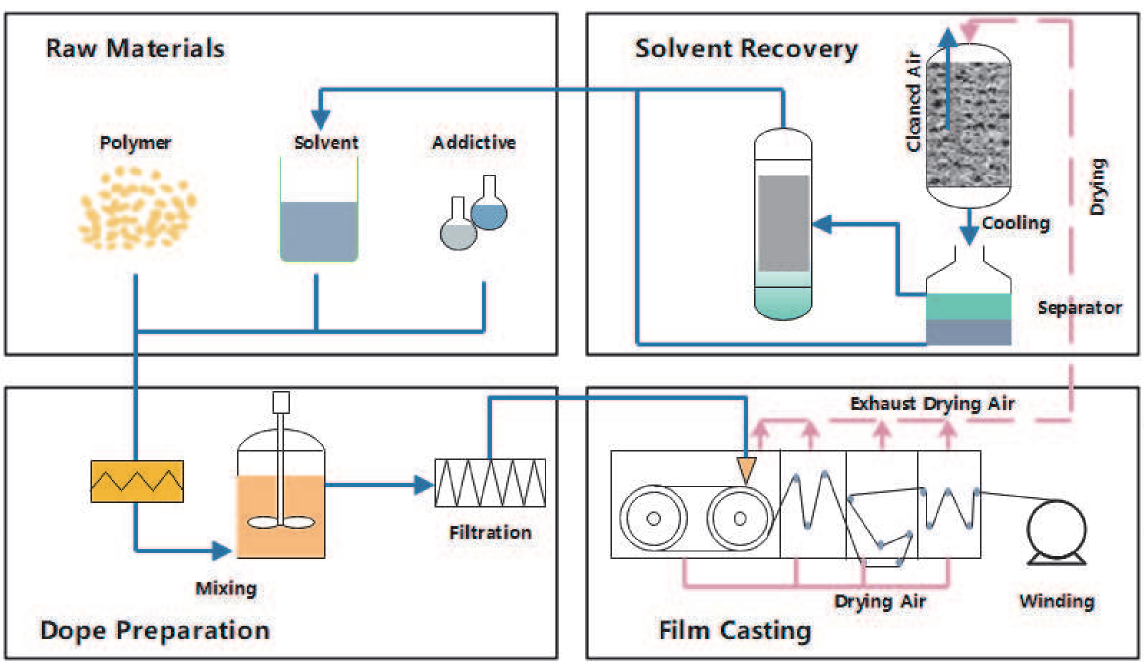



**Figure 1.**
*Production of solvent cast films, adopted from [47].*

most cases, the temperature of the imidization process needs to reach 300–350°C [55], under which, even in a vacuum or inert atmosphere, the PI system is prone to discoloration. At the same time, microdefects such as pinhole cracks are also prone to occur during the dehydration process. Therefore, in the preparation process of the colorless PI film, the PAA route is rarely used. The organo-soluble PI solution is only applicable to polyimides that can be dissolved in organic solvents. This method uses a stable high-solid polyimide solution to form a film on a clean substrate.

Because the curing process of the pre-iminated PI solution is almost a pure physical process of solvent evaporation, the curing process can be realized under a lower temperature (≤250°C) which will not cause coloring. CPI films prepared this way will have a good surface smoothness and better transparency.

The excellent performance of PI film is related to its heteroaryl molecular structure as well as their unique production technology. Compared with laboratory preparation, industrial production also use the solvent casting process, however, the biggest difference between them is the stretching process. There are two stretching methods, uniaxial stretching (machine direction, MD) and biaxial stretching (transverse direction, TD, and mechanical direction, MD) technologies, as shown in **Figure 2** [56]. Biaxial stretching is always used to ensure the evenness of the film. The gelation of the PAA membrane used for stretching can be achieved by partial evaporation of the solvent, or by chemical treatment of the dehydrating agent (acetic anhydride, dicyclohexylcarbodiimide, etc.) and its catalyst (pyridine). During the stretching process, whether it is uniaxial stretching or biaxial stretching, the gel-like PAA film will lead to a complete orientation and stretching of the PI molecular chain. From the perspective of polymer physics, stretching will greatly improve the mechanical properties of the resulting PI film. CPI films produced by biaxial stretching have good optical transparency, heat resistance, and reduced dimensional change.

In production, the monomer of polyimide is firstly sent to a polymerization reactor for polycondensation to obtain PAA solution. The solution is degassed and casted to a continuous film on a heated, rotating steel drum forming a self-supporting PAA film. The gel-like PAA film will be peeled off from the metal drum and stretched in the machine direction (MD) and lateral direction, which is performed at a temperature of about 350°C to promote the imidization of PAA. This method above has been widely used in the preparation of polyimide films industrially. Whereas, due to the high temperature (350°C) of full imidization of PAA, the above-mentioned manufacturing process may be difficult for producing colorless polyimide film. Therefore, a novel manufacturing technology has been developed in recent years. It uses soluble PI resin as the starting material instead of PAA. The key elements of this procedure include the following: (1) the PI resin must be soluble in volatile solvents; (2) the formed PI solution should be stable with a reasonable solids

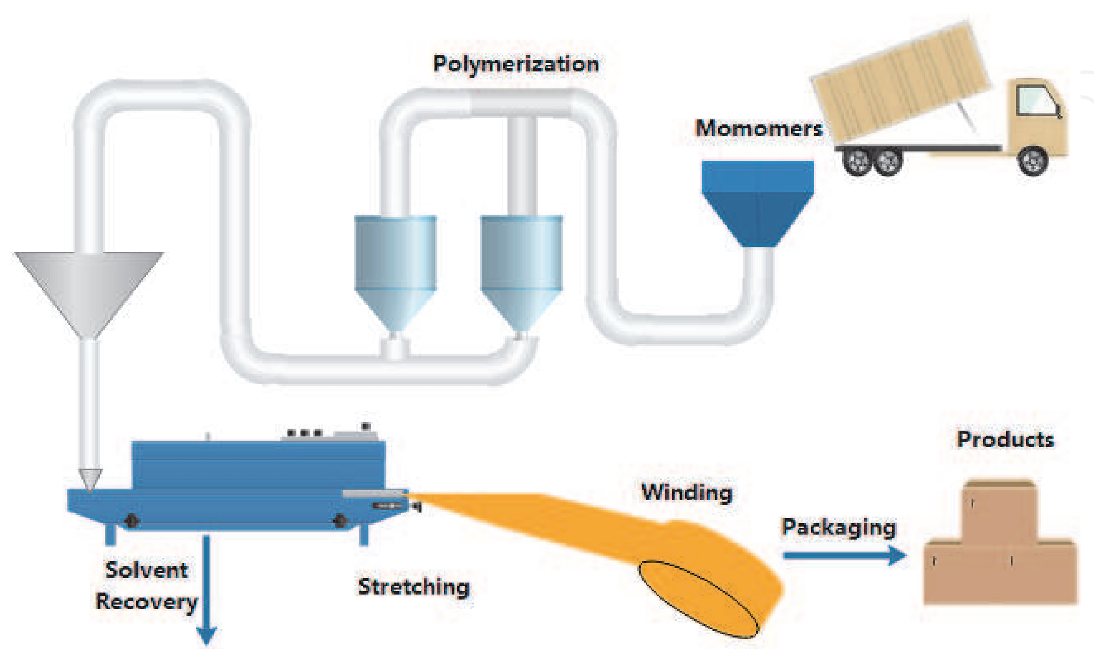



**Figure 2.**
*Production process of polyimide films, adopted from [56].*

content and viscosity; and (3) it must be able to form a uniform film and be releasable from the casting support. Mitsubishi Gas Chemical Company introduced a method [57, 58] for producing colorless and transparent PI films using this technology. The starting soluble PI resin was prepared from 1,2,4,5-cyclohexanetetracarboxylic dianhydride and aromatic diamine by one-step high-temperature polycondensation. The PI film was then stretched 1.01 times in the machine direction and 1.03 times in the transverse direction under the condition of nitrogen at a temperature of 250°C and dried. The obtained PI film showed good properties, with a thickness of is 200 mm, a light transmittance 89.8%, and a yellow index 1.9.

The major challenge of polyimide film market is the high level of technical capabilities involved in the film processing. Besides, the strong heat and chemical resistance of polyimide lead to processing difficulties, such as lack of solubility. This makes it difficult to integrate other materials into the polymer matrix. At the same time, there are some other key issues in processing of CPI film, high unevenness, the thickness decline caused by high stress (50–60% of the deposited value), and poor adhesion.

## 4. Challenges and solutions

### 4.1 Challenges of CPI for TaFEs

Targeting the applications of transparent and flexible electronics, it is of priority that CPI film owns satisfied optical, mechanical, thermal, chemical, optical, and electrical properties. For the key applications, the specifications of such properties are listed in **Table 1**. Like other materials, usually, the physical and chemical properties of CPI film are not independent; it is always the case that we need to adjust the composition and structure of the CPI film to balance the needs of the properties. However, there are major challenges we have to take, with the consideration of balancing the overall performance of the CPI film (**Table 7**).

### 4.2 Balance of the desired properties of CPI film for TaFE applications

Extensive studies have been made to improve the transmittance of CPI film. The major strategies to improve the transmission properties of light with the balance of other properties are by employing fluorine containing monomers [63–67], aliphatic monomers [68, 69], non-coplanar monomers [70, 71], adjusting conjugated

| Specification | Parameters | Desired figures | Reference |
|---|---|---|---|
| Transmittance | Transmission of visible light around 400–700 nm (T) | ~90% | [59] |
| Thermal expansion | Coefficient of linear thermal expansion (CTE) | <30 ppm/°C (as low as the inorganic components) | SiNx gas barrier (5–15 ppm/°C) [60] |
| Oxygen permeability | Water vapor transmission rate (WVTR) | $<10^{-5}$ $cm^3/m^2$ day at 23°C (OLED) | [61] |
| Water permeability | Oxygen transmission rate (OTR) | $<10^{-6}$ $g/m^2$ day at 23°C (OLED) | [61] |
| Thermal stability | $T_g$ | ~300°C (process temperature of α-Si TFTs is below 300°C) | [62] |

**Table 7.**
*The specifications of CPI film for transparent and flexible electronics.*

electrochromophores which limit the formation of charge transfer complex [72]. The influence of these monomer molecular changes on the transmittance and thermal stability can be observed more clearly in PI with a similar structural unit [11] (**Figure 3**). As shown in **Figure 3**, introducing fluorine atoms, alicyclic moieties, and flexible main chain is a very effective way to improve the transparency of CPI. The transparency will grow with more of these groups added into the molecule. However, the thermal stability decreases fast with the increase of the transparency of CPI, which is what the researchers have tried for years to overcome. With the deepening of the research of CPI, a unique kind of monomers-isomerized monomers have drawn people's attention. **Figure 4** has shown that changing a CPI monomer to an isomerized one will enhance not only the transparency of the CPI but also the thermal property, which is different from other CPI monomers [73]. This means this kind of noncoplanar structure have no or less influence in the rigidity, and therefore will not sacrifice the mechanical and thermal properties. So it is suggested that using the noncoplanar in the main chain as well as bringing in fluorine atoms, alicyclic groups in the molecular design may be a very useful way to achieve a better comprehensive performance under the synergistic action of all the factors.

As discussed in the previous section, it is very promising to obtain CPI with good mechanical and thermal properties by using noncoplanar structure cooperating with fluorine and alicyclic groups. But these factors are associated with negative effects to the applications as gas barriers and transparent packaging materials. They will lead to worse water/oxygen permeability, even though the water/oxygen permeability is always a pain point of CPI. The usual methods to solve this problem is coating barriers like $SiN_xO_y$ [74] and $Al_2O_3$ [75] or using composite fillers like graphene [75], montmorillonite [76], and other nanosheet fillers. Nanocomposite filler method is more practical in industrial production and can reduce the thermal expansion of CPI while keeping its transparency and thermal properties, so it is a more promising way in the future.

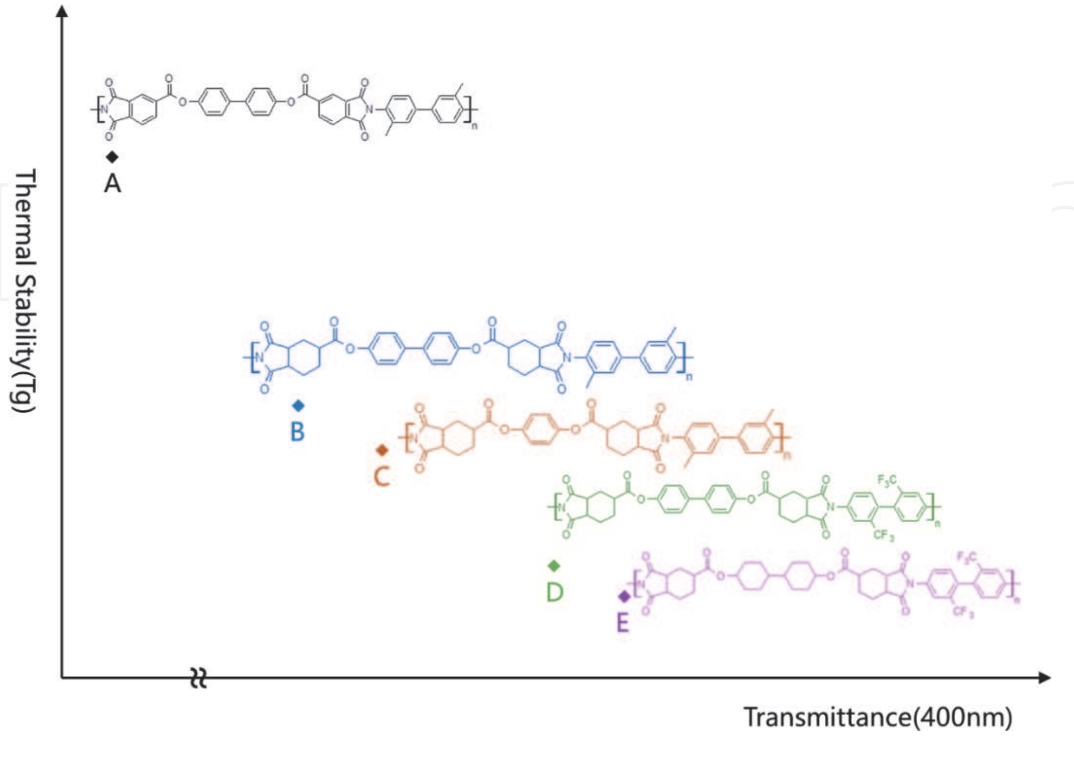



**Figure 3.**
*The molecules of CPIs with a similar structure but different transmittance and thermal stability, which suggest the influence of the main chain, fluorine atoms, and alicyclic groups.*

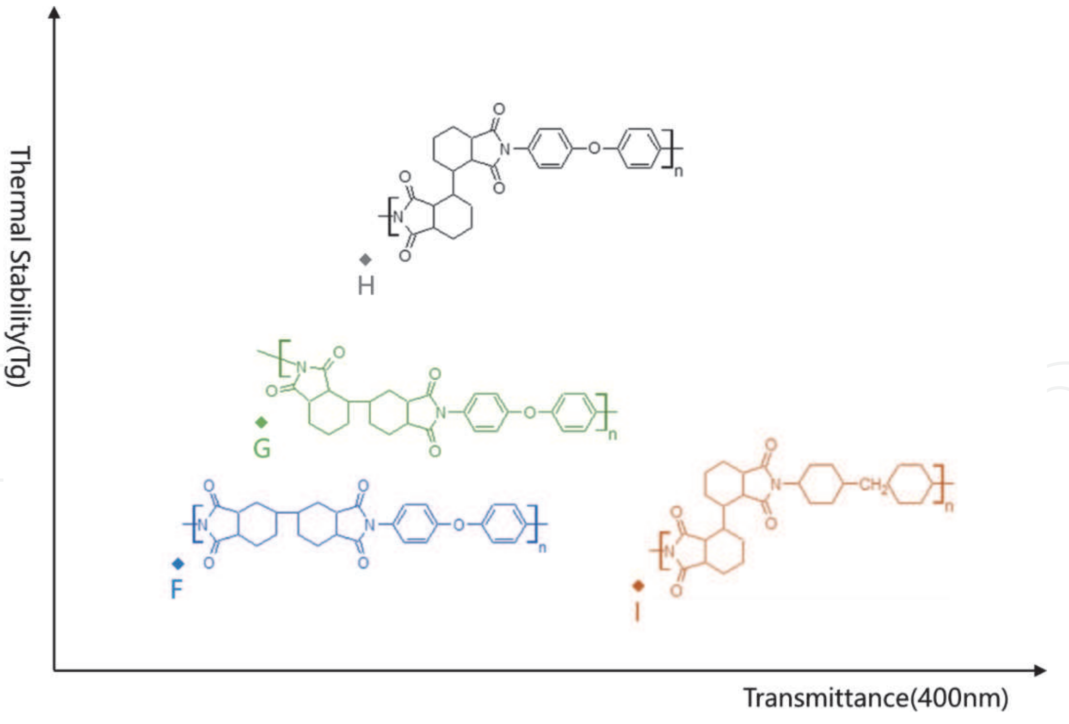



**Figure 4.**
*The molecules of CPIs with isomeric structures have different transmittance and thermal stability.*

In general, it is thought prospective to produce CPI with high comprehensive performance by using nanosheets as the filler to modify CPI with good thermal and mechanical properties. This kind of PI can be prepared by using the noncoplanar in the main chain as well as bringing in fluorine atoms, alicyclic groups.

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