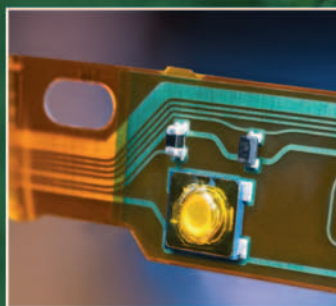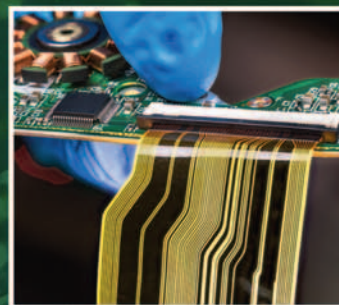# POLYIMIDES

ADVANCES IN BLENDS AND NANOCOMPOSITES

EDITED BY
MARIANA-DANA DAMACEANU
RALUCA NICOLETA DARIE-NITA

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Advances in Blends and Nanocomposites

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Contents

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Polyimides: Past, present, and future

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1. Introduction

The polymer material development over the time has been constantly triggered by the emerging technologies needs that required performance improvements like weight reduction, energy saving, lower cost, in general, and in particular, depending on the application, thermal and chemical stability, high mechanical strength, flexibility, durability, etc. The genesis of polyimides (PIs) was a milestone in the evolution of 20th century technology, due to their capability to meet all these demands and use in a large library of products. As one of the most attractive high-performance polymers, PI found applications in various domains, from aerospace and defense, to engineering field and medical industry, contributing to the technological revolution and human society evolution. The outstanding properties and versatility of PIs, unparalleled by any other class of polymers, led to a well-established reputation (Sroog, 1991; Hergenrother, 2003), so that the PI is considered today a material imperative for majority of applications and, especially, for those where heat and chemical resistance is a must.

PI was nominated as a high-performance polymer due to its physico-chemical characteristics like thermal stability, mechanical strength, chemical robustness and radiation resistance, which are preserved under extreme conditions, for example, high/low temperatures. In contrast to the

conventional engineering plastics, PI displays tight bonds provided by the resonance-stabilized aromatic rings and heterocyclic units within the macromolecule that along with the chain rigidity, crosslinking structure, crystallinity, strong intermolecular forces, and high degree of structural planarity explain their superior performance and capability for long-term service in harsh environment (Thiruvasagam, 2013; Xu et al., 2021). Apart from this, symmetrical carbonyl groups from the conjugated imide system restrict the mobility of free electrons, leading to outstanding electrical insulation ability, that along with the low moisture absorption made PI an ideal dielectric material in electronic insulation applications in aerospace, microelectronics, transportation, and also in power industries for insulated cores (Ma et al., 2019; Ogbonna et al., 2022).

Unfortunately, all these come bundled with inconvenient processing characteristics owing to their poor or insolubility in common organic solvents and melting at elevated temperatures (Damaceanu et al., 2009; Bruma et al., 2009; Constantin et al., 2021a). With the main goal of enabling advancement of industries such as aerospace engineering, defense, and electronics, these drawbacks busted large efforts toward processability improvement without adversely affecting its beneficial properties, like excellent thermal stability and low dielectric constant. Thus, the PI solubility and other properties were flexibly tuned by molecular or structural changes, for example, a conventional PI film can be converted into a colorless and transparent one by variations in the chemical structure (Damaceanu and Bruma, 2015). However, the most challenging aspect is to find a compromise between solubility, molecular weight, thermal stability, mechanical characteristics, and dielectric properties. For instance, by the introduction of rigid segments into the main chains, such as benzene rings or heterocyclic units, the thermal stability can be considerably improved at the expense of a lower solubility and difficult processing. Conversely, the solubility and processability of PIs can get better by insertion of flexible bonds between aromatic units or by attaching aliphatic groups, but, in turn, these will lead to a reduced thermal stability. Therefore, it is necessary to carefully balance all these

characteristics according to the needs of the addressed application (Abadie, 2012).

The structural alteration of the classical PI structure provides multiple possibilities for its development in various advanced applicative fields. Through molecular engineering, rigid aromatic units can be combined with flexible segments like $-O-$, $-S-$, $-CH_2-$, $-SO_2-$ into the same polymer chain, resulting in chain flexibility, segmental mobility modulation, and improved solubility and processability but lower glass transition temperatures (T_g). When bulky trifluoromethyl ($-CF_3$) groups are incorporated into PI structure, the free volume increases, thereby improving several properties of PIs, such as increased solubility and lowered dielectric constant without losing the thermal stability. The introduction of aliphatic/alicyclic units in PI main chains is known as one of the most efficient methods to lower the dielectric constants (k) and improve optical transparency, while noncoplanar or kink structures, as well as spiro centers, can prevent a tight chain packing and hamper the appearance of efficient charge transfer complexes (CTC), thus leading to excellent solubility and other profitable performances. The cardo moieties can also lead to colorless transparency and improved thermal properties. The substitution of symmetrical segments with unsymmetrical ones can reduce the chain packing and the strength of interchain interactions toward superior solubility, melt processability, and other useful characteristics (Ghosh et al., 2012; Zhuang et al., 2019). Upon chemical modifications, PIs may win new characteristics that can induce attractive applicative perspectives and enable the development of novel products. For instance, poly(amide-imide) (PAI) is a thermoplastic PI with superior mechanical strength, thermal, and oxidative stability. Fluorinated PIs are good candidates for optoelectronics and solar cells due to their transparency or controllable light transmittance. There are multiple other functional PIs whose application can be tailored function of the monomers used in the synthesis, for example, electrochromic (EC) PIs, photosensitive PIs, shape memory PIs, thermoset or thermoplastic PIs, etc (Sezer Hicyilmaz and Celik Bedeloglu, 2021).

However, when the preparation of the new monomers is too tedious, a feasible way to optimize the PI structure toward better performances consists in the copolymerization utilizing existing monomers as raw materials. Alternate copolymerization has the great advantage that can provide PI materials with different spatial arrangements and tailored properties for desired applications, such as solubility, glass transition temperature, durability, adhesion, chemical resistance, crystallinity, etc. through monomers ratio control (Damaceanu et al., 2011; Sava et al., 2018; Butnaru et al., 2021). When a single PI cannot satisfy the necessity of a specific application, blending it with another polymer can be approached to tailor the properties of PI materials. The resulting blend materials are engineered to display the positive features of both polymers while attempting to quench the negative features. The morphology and physical properties of the blends are controlled to a large extent by the miscibility and phase behavior. While a miscible polymer blend is a homogeneous, single-phase material and behaves as a single entity, an immiscible blend contains two distinct phases and is naturally heterogeneous. Occasionally, complete miscibility or immiscibility may not be desired in blends, but instead, some intermediate states may endow the PI material with the expected properties (DeMeuse, 2014).

With the evolving nanotechnology field, PI materials had to face new issues, for example, to organize themselves or to respond to external stimuli, which triggered the development of new PI materials capable of long-term maintenance of their high-performance characteristics under high or very low temperatures, chemical reagents, radiation, and other harsh factors. A feasible and economic way to mitigate this problem appeared to be the development of composite materials based on PI matrices. There are numerous examples of PI nanocomposite materials filled with carbon nanotubes (CNTs), graphene oxide, carbon fibers, metal oxides, graphite etc., and their physico-chemical characteristics have been reported. Enlarging the library of PI matrices and varying the type and amount of the nanostructured material enabled obtaining diverse PI nanocomposites. By integrating the two complementary

benefits, PI-based composites strongly expanded the applications, especially in aerospace, microelectronics, catalysis, energy, sensors, and separation membranes (Ma et al., 2023).

2. Brief history of PIs

The aromatic PI was discovered in 1908 by Bogert and Renshaw (Bogert and Renshaw, 1908), when they obtained a polymer from 4-amino-phthalic anhydride, but the first commercial PI was not obtained until 1951, when Windfoot Co. patented the synthesis of PI using phthalimide salt and acyl chloride (Flory, 1951). Almost 50 years later (in 1955), Edwards and Robinson prepared for the first time a high-molecular-weight semialiphatic PI by polymerizing the pyromellitic salts of aliphatic diamines (Edwards and Robinson, 1955). The genesis of the first aromatic PI obtained by the two-step polycondensation reaction dates from 1965 (Endrey, 1965). This polymer has been patented by DuPont under the tradename Kapton HN, and very soon after, the industrial-scale production of Kapton started. Due to the remarkable thermal stability (>500C), mechanical behavior (Young's modulus >2 GPa, tensile strength >70 MPa), and chemical stability, the Kapton PI become over the time one of the most performant polymer among PIs used in various applications. Initially, three types of "Kapton" films were commercialized: H−, F−, and V-type, and after that, various specifications of three types and new ones were produced (e.g., Kapton CRC—tough film that exhibits an excellent balance of physical, chemical, and electrical properties over a wide temperature range, particularly at unusually high temperatures; Kapton MT + — PI films with superior thermal conductivity of 0.8 W m^{-1}·K^{-1}, available as thin as 38 μm up to 127 μm, which lowers operating temperature by 20−45°C in e-motors as an NKN slot liner and increases power output by 10%−30% for PTC heaters) (DuPont, 2023), so that the modified PI films have accounted for 85% of the total production of PI films.

Until today, the method using polyamidic acids (PAAs) as precursors was used to synthesize versatile aromatic PI structures, which found applications as films, coatings,

automotive parts, filtration membranes, catalyst supports, or gas separation membranes, among others. However, the poor solvent processability of PIs inevitably increases the processing cost, so that researchers had to find solutions to mitigate this issue. Thus, poly(ether-imide)s (PEIs) as a special subclass of PIs were invented, the first commercial PEI under the trademark Ultem being patented by General Electric Co. in 1975 (Heath et al., 1974). Besides the ether linkages, other important alteration of the PI chemical pattern consisted in the incorporation of amide units, resulting in -PAIs. PAIs were first developed at DuPont in 1955, and 5 years later, they were commercialized by Standard Oil of Indiana (Amoco; now Solvay Advanced Polymers) under the trade name Torlon (Stephens, 1966).

After the success of these tradename PIs, new PI derivates and more sub-groups of PIs were further developed. Among all their structural elements, the greatest characteristic shared by most PIs was the aromatic chain, while the only significant difference arose from the chemical modification of the aromatic backbone groups. Thereafter, the variation in the processing methods of PIs resulted in versatile PI materials that now are commercialized all over the world.

3. Synthesis of PIs

Aromatic PIs can be obtained by various methods, the most commonly used being the polycondensation reaction of aromatic dianhydrides with aromatic diamines in polar aprotic solvents (Scheme 1.1), which generally leads to infusible and insoluble polymers. The synthesis takes place in two steps, with the formation of the intermediary PAA at room temperature in the first step, which is then subjected to a cyclodehydration process in the second step. The later can be performed thermally (in solution or film) or chemically (in solution) (Aguilar-Lugo et al., 2012; Yi et al., 2016).

The single-step polycondensation reaction is usually approached when the monomers are not soluble at room temperature in the selected solvents, but became soluble by heating, or display low reactivity. For instance, six-membered PIs such as polynaphthylimides and
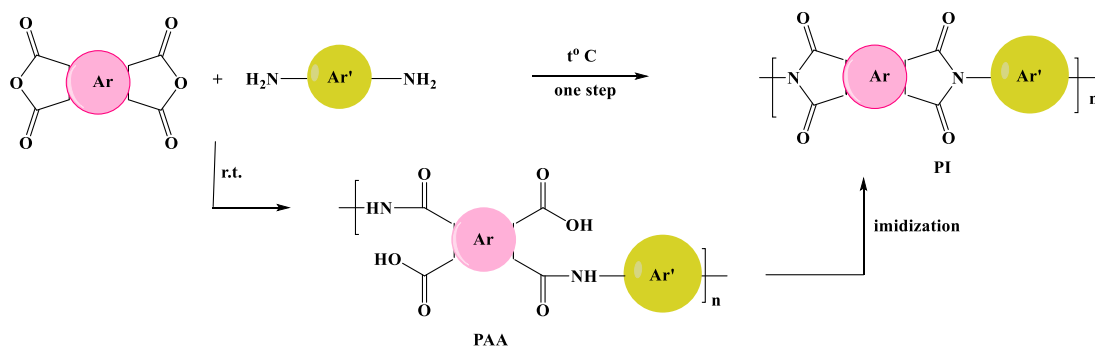
Scheme 1.1 Polycondensation reaction of aromatic dianhydrides with aromatic diamines toward polyimides (PIs).

polyperyleneimides are obtained by this pathway due to the insolubility of naphthalene- and perylene-based dianhydrides in polar solvents at room temperature (Vinogradova et al., 1970; Damaceanu et al., 2012). The process implies heating of a stoichiometric mixture of monomers in a high boiling solvent (nitrobenzene, *m*-cresol, and dipolar aprotic amide solvents) at 180−220°C, often in the presence of a catalyst (quinoline, tertiary amine, carboxylic acid, etc.). The imidization still proceeds via the PAA route, but the amount of PAA at any time is very low.

The reaction between cyclic dianhydrides and primary diamines occurs following an SN_2Ac mechanism (bimolecular nucleophilic acyl substitution), which consists of the nucleophilic attack of the amino group at the carbonyl carbon atom of the dianhydride moiety, when PAA is formed, which is afterward converted to PI by dehydration. Since this reaction requires the use of high polar aprotic solvent, an inevitable process after PI formation is to remove it. The cyclodehydration may take place by a chemical or thermal treatment, with the release of water molecules. PAA is obtained in an equilibrium reaction that starts with the formation of a CTC between dianhydride and diamine. There are several factors that influence the molecular weight of PAA, among which the purity of the monomers, their reactivity, the stoichiometric equilibrium, as well as the selected solvation medium are the most important (Sroog, 1991). The polymerization reaction can be carried out in dipolar aprotic solvents, such as dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), or dimethylformamide

(DMF), which can form hydrogen bonds with the carboxyl group, thus strengthening the balance toward the formation of PAA.

With respect to the imidization process of PAA to PI, there are several available methods. The most common is the thermal pathway that can be applied both in solution and in solid state. In solution, the cyclodehydration can be performed at temperatures between 160 and 200°C, being preferred compared to the solid-state imidization that takes place at higher temperature due to the possibility to avoid secondary reactions that can be present during film imidization. However, this method is useful when the final PI remains soluble in the reaction medium and allows further processing by wet methods. To remove the resulting water during the conversion of PAA to PI in solution, the cyclodehydration process is conducted at a temperature up to 180°C in the presence of an azeotropic forming agent, such as 1,2-dichlorobenzene, xylene, or cyclohexyl-pyrrolidone, or by using a strong stream of nitrogen to be able to carry the water vapors out of the system (Kim et al., 1993; Ghosh et al., 2012; Chiriac et al., 2020).

When PIs are targeted in form of free-standing films, coatings, or other solid forms, the thermal imidization is carried out on the PAA processed into the desired form, under a programmed temperature regime set between 25 and 300°C, as to enable the formation of defectless products (Ghosh et al., 2012). This process allows a maximum conversion of about 92%−99% of PAA into the corresponding PI. Due to the rigidity of the macromolecular chains, uncontrolled molecular weights, or crosslinking occurring during the imidization process, most aromatic PIs obtained by solid-state thermal imidization are insoluble and infusible and possess low or no processability, which is highly required by most applications (Mittal, 1984).

Another possibility to convert PAA into PI consists in using chemical agents, a method that is less preferred due to the toxicity of reagents. Acetic anhydride, propionic anhydride, or *n*-butyric anhydride may be used as dehydrating agents in the presence of a basic catalyst such as pyridine, triethylamine, or isoquinoline. Among these, the mixture

of acetic anhydride and pyridine is the most commonly used (Kailani and Sung, 1998). However, chemical imidization has the additional disadvantage that often requires thermal treatment of the obtained PI powder at temperatures of about 300°C to complete the imidization and remove the solvent traces.

For the synthesis of PIs, diamines were occasionally replaced by diisocyanates and allowed to react with dianhydrides. Several mechanisms were proposed for this reactions, among which can be mentioned the formation of a seven-membered ring and carbon dioxide (CO_2) as the intermediate and the by-product or the hydrolysis of isocyanate when, function on the degree of hydrolysis, amine or urea is generated, followed by the condensation reaction with dianhydride (Kim et al., 2023).

Polyimide as coating was synthesized in vapor phase by allowing in a mixing chamber separate vapor streams of diamine and dianhydride to come in contact at high temperature, followed by pushing the mixed monomer vapors onto a film target. This method was successfully applied for the synthesis of some PIs based on pyromellitic dianhydride or trimellitic anhydride acid chloride, using Kapton or polyethylene therephthalate substrates, when PIs or PAIs with lower oxygen permeabilities were obtained compared to conventionally prepared coatings (Sroog et al., 1965).

PIs were also obtained by transimidization reaction, which was first reported by General Electronics Co. in 1974. By masking the dianhydride with an electron−acceptor amine (e.g., aminopyridines) and then mixing the formed diimide with electron-donating diamine (e.g., *m*-phenylene diamine), PIs with reasonable molecular weight can be obtained following a similar mechanism to the conventional "two-step" reaction of dianhydrides with diamines, with the resulting amide polymer undergoing an imidization process (Xu et al., 2021).

In the conventional "two-step" imidization, the used monomers are sensitive to water (e.g., dianhydrides) or oxygen (e.g., diamines), and since monomers purity is crucial for achieving high molecular weight PIs, an alternative

pathway was developed, namely aromatic nucleophilic substitution. This method allows using stable monomers under normal conditions with high reaction rate at low temperatures ($<100°C$), making the cost of synthesis to lower to some extent (Eastmond and Paprotny, 1996). For this purpose, a leaving group (e.g., F, Cl, Br, NO_2) is attached to the phthalic anhydride derivative. Under the attack of a phenolic derivative, a Meisenheimer complex intermediate is formed, that further enables the generation of the ether linkage. This method that uses monomers with preformed imide rings is widely used for the synthesis of PIs with bulky/cardo units, with the scope to improve solubility in organic solvents and reduce the color (Mushtaq et al., 2017).

Alternative methods were applied for the preparation of PIs such as solid-state and aqueous synthesis without the use of toxic organic solvents like N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), or N,N-dimethylacetamide (DMAc). By thermal treatment of physically mixed amine and anhydride monomers at a high temperature, in the absence of solvents, eco-friendly PIs were obtained by solid-state condensation (Chu et al., 2012), when anhydride precursor undergone melting and reacted with the neighboring amine monomers to form an oligomer that was further subjected to imidization. Other methods involved mechanochemistry to prepare PIs, when PAA was obtained by using ball milling and then thermally converted to PIs (Rensch et al., 2022). Aqueous-based PI synthesis was accomplished using a tetracarboxylic acid and diamine monomers in distilled water under a small positive pressure of 20 psi (0.14 MPa). The PI precipitated in form of an ammonium salt that was further heated to $180°C$ to dehydrate and obtain the PI material (Chiefari et al., 2003). Recently, the one-pot synthesis of PIs was reported in aqueous media by a hydrothermal method, which involved elevated temperature and pressure conditions in a closed vessel (Baumgartner et al., 2015). Despite the great advantage provided by aqueous syntheses of PIs, their potential for industrial production is rather low and requires further improvements.