POLYIMIDES

1. Introduction

The first reported synthesis of an aromatic polyimide was in 1908 (1). However, much of the credit for the development and commercialization of polyimide products goes to DuPont, who benchmarked this endeavor in the 1960s with the release of Kapton® H film, Vespel® molded parts and Pyre-ML® wire varnish (2). This effort inspired other researchers in academia, industry and government labs to pursue the chemistry, fabrication and applications of polyimides not envisioned several decades ago. There are several excellent books and review articles that address the extensive topic of polyimides (3–8). This text provides an overview of the field of polyimides from synthesis and basic kinetic behavior to fabrication and articles of manufacture.

2. Polyimide Synthesis

The synthetic approach to the formation of polyimides is divided into three groups. The first group involves the synthesis of the polyimide by increasing the molecular weight of the monomer(s) through the formation of the imide ring via the amic acid/ester route. The second approach involves increasing the molecular weight of a precursor already containing the imide ring. The last method involves the conversion of a polymer into a polyimide. The requirement is that these approaches must be based on high yield organic reactions.

2.1. Polyimides via Imide Ring Formation - Chemistry. The two-step approach is the most general approach used in the synthesis of linear polyimides (9–12). The first step involves the treatment of a diamine either with a dianhydride (the most popular), a tetracarboxylic acid, a diester diacid, a diester diacid-chloride or a trimellitic anhydride chloride (TAC) as in the case of polyamide-imides (Amoco's Torlon$^{®}$) (13,14). These reaction schemes are generally carried out in a high boiling polar protic (phenolic) or aprotic (NMP, DMAC, DMF, etc.) solvent at low to moderate temperatures, resulting in the formation of the polyamic acid (or polyamide acid), amic ester, amic acid ester, etc. via nucleophilic attack by the amine on the carbonyl carbon (15). Next the formation of the imide ring is formed through thermal treatment, chemical dehydration or both by a second nucleophilic attack, occurring at the adjacent carbonyl carbon, by the amide nitrogen, followed by the elimination of a condensate (typically water or alcohol). Removal of this condensate forces the equilibrium toward the right, driving the polymerization to completion (Le Chatelier's principle), thus forming the imide ring (10,16). Alternatively, a "one-step" method or direct conversion is used where a diamine and a dianhydride are placed in a solvent and heated to a temperature where the formation of the amic acid moiety rapidly dehydrates to the resulting imide. Thus, the polyimide is formed in "one step" (17).

2.2. Polyamic Acid Formation. To successfully carry out this synthetic approach, the following requirements must be met: chemical purity; the proper type and percent solids of reaction medium (facilitating solubility of the resulting polyamic acid); reaction temperature; and a method allowing for the removal of any by-products of polymerization (heat, condensates etc) (16, 18). Most commonly, a bi-functional compound is treated with a diamine to afford the amic acid or amic ester, followed by imide ring formation during the final polymerization step. The routes to achieving a high molecular weight polyimide starting from the monomers via the polyamic acid are shown in the reaction diagram in Figure 1 (19). When a diamine (I) is treated with either a dianhydride (II), tetraacid or diacidester (III), alternative routes may occur depending on the reaction kinetics, where k_1 and k_3 are desirable and k_2 and k_4 are not. Table 1 summarizes the approximate kinetic "k_x" values. The pathway to k_4 depends on: the amount of water or alcohol in the reaction medium; the reactivity (electrophilicity) of the dianhydride or tetraacid/diacid-ester; and the nucleophilicity of the diamine (Table 2). Steric hindrance and isomerization; polarity and autocatalytic effects of the solvent; and the time/temperature profile during the polyamic acid formation also affect the pathway to k_4 (21–23). Conversion of the anhydride moiety, k_4, has the effect of introducing another chemical functionality with a different reactivity that can affect both k_1 and k_3 via resonance. As shown on the Reaction Coordinate (Figure 2), the effect of k_2 competes with k_1 and k_3 when the reaction temperature is raised and the thermal dehydration k_5 conversion to imide is occurring. Once the imide ring is formed, depolymerization

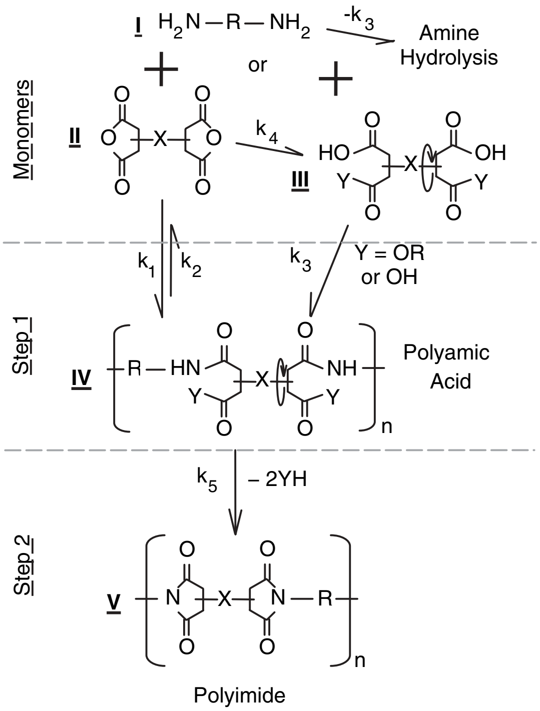


Fig. 1. Reaction diagram for thermal imidization via polyamic acid/ester.

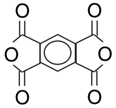
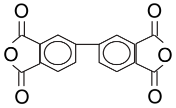
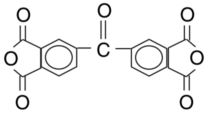
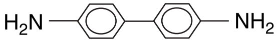
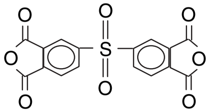
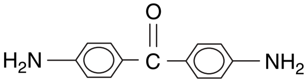
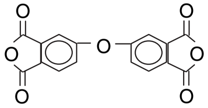
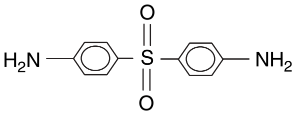
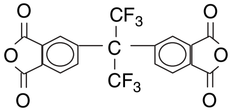
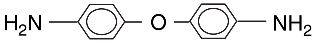
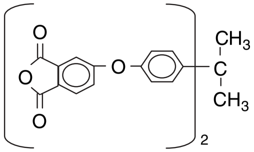
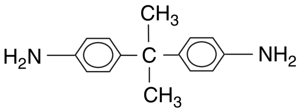
is severely limited through removal of the condensate by-product. The choice of diamine and dianhydride affects the rate of polyamic acid formation both sterically, and through the electronic interactions of the monomers (24–26). PMDA is the dianhydride with the highest Ea value on Table 2. Any diamine that is treated with PMDA should polymerize faster than if it is treated with a dianhydride having a lower affinity. However, once one of the anhydride units of PMDA has reacted, the second anhydride will display a lower reactivity because the former anhydride group has less electronic withdrawing ability since it no longer exists. This effect on other dianhydrides is less pronounced as the anhydride groups are separated by additional moieties that decrease the impact of the reacted anhydrides (21). A similar trend is seen with diamines. The more basic the amine, the faster it can react with a moiety that is susceptible to nucleophilic attack.

Table 1. **Typical Rate Constants for Polyamic Acid Synthesis**[a]

Reaction	Rate Constants
propagation (k_1)	$0.5-6.01\ \mathrm{mol^{-1}\ sec^{-1}}$
depolymerization (k_2)	$10^{-5}-10^{-6}\ \mathrm{sec^{-1}}$
imidization (k_5)	$10^{-8}-10^{-9}\ \mathrm{sec^{-1}}$
anhydride hydrolysis (k_4)	$0.1-0.41\ \mathrm{mol^{-1}\ sec^{-1}}$
amine hydrolysis ($-k_3$)	$0-10^{-6}\ \mathrm{sec^{-1}}$

[a] Refs. 21.

Table 2. **Electron Affinity and Basicity Values of Several Common Dianhydrides and Diamines Used in the Synthesis of Polyimides**[a]

Diahydride	Abbr. Name	E_a(eV)	Diamine	Abbr. Name	pKa (H_2O)
	PMDA	1.9		pDA	6.08
	BPDA	1.38		mDA	4.08
	BTDA	1.55		DAB	4.60
	DSDA	1.57		DABP	3.10
	ODPA	1.30		$DDSO_2$	2.15
	6FDA	ND		ODA or DAPE	5.20
	BPADA or ULDA	1.12		Bis-DA	ND

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[a] Ref. 5, 23.

ND=Not Determined.

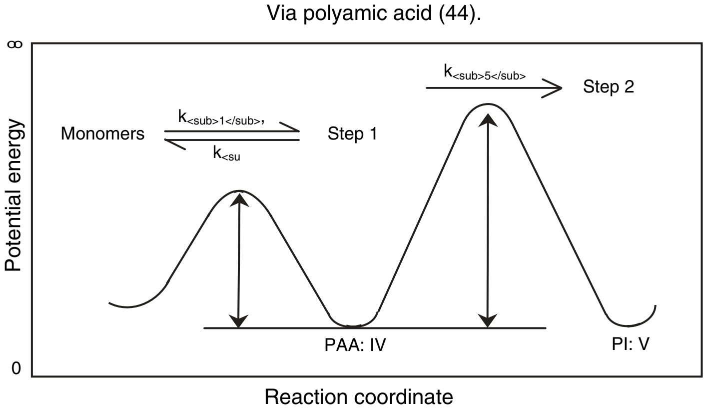


Fig. 2. Qualitative reaction coordinate diagram for polyimde synthesis via polyamic acid (52).

Additionally, depending on type, the larger the amount of chemical groups separating the amines, the less of an effect the conversion of one amine will have on the reactivity of the other (27).

Solvent effects depend on several factors, including, the polarity of the medium: the percent solids; and the solubility of the reactants. As the polarity of the medium changes with conversion to polyamic acid, the visosity and potential autocatalytic effects (kinetic conversion to polyamic acid) are observed (28). These effects are caused by the increasing molecular weight of the polyamic acid, that results in the buildup of carboxylic acid. The hydroxyl portion of the amic acid can form additional hydrogen bonds to adjacent polyamic acid groups, artificially increasing the observed viscosity (12,16). These additional carboxyl acid protons can assist nucleophilic attack (on the carbonyl carbon) via coordination with the anhydride carbonyl oxygen increasing the step growth kinetics to polyamic acid formation. An accurate kinetic profile has been difficult to obtain as a result of the solvent effects and the changing reaction medium. Some investigators claim that irreversible second order kinetics is followed, while others have observed reversible autocatalytic kinetics when THF is the solvent. Typically, polymerizations carried out in amide solvents (polar aprotic) do not display autocatalytic behavior (25,26). These solvent molecules closely associate with the hydroxyl protons, effectively isolating them from interacting with other anhydrides and amic-acids. The reaction rate generally increases as the solvents become more polar and more basic (29,30). A model compound study showed that the acylation rate increased from THF $<$ acetonitrile $<$ DMAc $<$ m-cresol. The polar protic solvent, m-cresol was claimed to increase the rate because it functions as an acidic catalyst (28,31). Similar observations were noted when acids (benzoic acid) were introduced into a polyamic acid medium employing an amide solvent. THF, not being very basic, does not associate with the polyamic acid and some reversal occurs. This “retro” reaction (k_2) occurs when a proton is transferred from a carboxylic acid to an amide nitrogen (or any other basic species), followed by the subsequent attack of the carboxylate oxygen on the adjacent carbonyl carbon to reform the anhydride or the rare isoimide (32,33). This reverse reaction can be suppressed by replacing the hydroxyl proton of the polyamic acid with amine salts or esters causing a marked decrease in conversion to monomeric species (12,34–36).

The effects of adventitious water on both the starting anhydride and polyamic acids has been shown to decrease their molecular weight over time via conversion to diacid and hydrolytic cleavage, respectively (12,19,37–39). This drop in molecular weight appears to be more dramatic the more dilute the solution. This may be caused by the apparent increase in water content as the percent polyamic acid decreases. Additionally, the conversion from polyamic acid to monomeric species is unimolecular, whereas the reverse reaction is bimolecular, shifting the equilibrium to the left towards the reactants (10). Evidence has indicated that further imidization of the polyamic acid occurs upon standing over time, at various temperatures, releasing water into the solution, resulting in further hydrolysis of the polyamic acid (12,19,40).

Lastly, monomer addition (sequence and rate) has shown to affect both thermodynamic equilibrium, and the resulting molecular weight of the polyamic acid. This condition is due to the difference in solubility of the monomers (dianhydride and diamine) in the polymerization solvent (10,19). As the dianhydride slowly dissolves in a medium containing the faster dissolving diamine, it maintains stoichiometric balance with the diamine, setting the condition for an infinite degree of polymerization. This "pseudo-interfacial" polymerization generates high molecular weight polyamic acid until one of the monomers is consumed. Thus, near the completion of the reaction, the medium contains a wide bimodal distribution. As the unreacted or excess monomer has time to come in contact with the high molecular weight polyamic acid, thermodynamic equilibrium (k_1/k_2) occurs and the molecular weights redistribute towards a unimodal distribution (41–43).

2.3. Polyimide Formation via the Polyamic Acid. The three methods to form the polyimide from the polyamic acid are thermal, chemical, and a combination of both. The thermal conversion of polyamic acid to polyimide requires the removal of the condensate produced during cyclodehydration (Figure 1). This is achieved by elevated temperatures and, whenever possible, the addition of a solvent that facilitates azeotropic removal of the condensate. A typical solution thermal conversion reaction setup contains approximately 30% solids polyamic acid in NMP, 10% solids xylenes (azeotrope to remove water), and the reaction temperature is maintained at about 165°C for several hours with water distilling out rapidly early in the reaction (10,44,45). Thermal conversion of polyamic acid in solution is fairly straight forward and only becomes complex when the resulting polyimide precipitates out of solution prior to complete imidization. The kinetics is more complex when the polyamic acid is isolated as a powder, spun as fiber, or cast as a film prior to imidization (46). Generally, the azeotropic co-solvent is not present in these "solid state" preforms, and the effects of the advancing Tg, solvent evaporation rate, the percent solids, steric effects, side reactions, cure temperature, and surface to volume ratio of the polymeric preform effect the overall kinetics (11,47–49). Thus, attempts to follow the imidization rates using spectroscopy have been confusing as these factors are difficult to account for. One reaction that does not occur during thermal imidization is crosslinking between diamide groups (50–52). This is not surprising since there are soluble polyimides cited in the literature, and no spectral evidence exists that supports this mechanism. However, thermal aging above 350°C for a period of time may result in crosslinking, but this is most likely due to a free radical mechanism (thermal degradation) and is influenced by film thickness, atmosphere and the casting surface (53–55). Two pathways of thermally induced imidization are: loss of proton on the carboxylic acid group after cyclization (the amide nitrogen initiates the attack on the adjacent carbonyl carbon); or removal of the proton on the carboxylic acid prior to or during ring closure. Since the conjugate base of the amide is more nucleophilic than the amide itself, ring closure should be faster in the latter case (11). When thermal imidization occurs in the presence of an amide solvent, the conversion to polyimide proceeds more readily, as the loss of amic acid proton is facilitated through solvent hydrogen bonding. In some cases, the rate of thermal imidization occurs in two steps (11,47). The first step is the rapid conversion to imide above 150°C, and the second step is a slower process during the latter stages of imidization. The following scenario can explain this. During the early stages of imidization, more solvent is present to assist ring closure and the Tg of the polymer is low (11). As the thermal conversion continues, the Tg is increased and the solvent content decreases (47). Chain mobility and solubility is decreased with increasing conversion, especially if the growing polyimide is semi-crystalline (56). Further depletion of solvent decreases the amount of solvent-polymer complexation that normally facilitates the rate of ring closure (11). This two-step rate effect is seen for fibers (high surface area) and cast films where solvent is lost during thermal processing. It has been shown that thicker films form imides at faster initial rates. These thicker films retain solvent longer, due to extended migration/evaporation time, allowing the chains more mobility and increased solvent complexation time to undergo conversion (57). However, the effects of the surface imidizing faster (skinning) than the bulk must be taken into account for thermal convection curing (19). Dry polyamic acid powders with the highest surface to volume ratio imidize the slowest. The resulting molecular weight of the polyimide depends, in part, on the molecular weight of the polyamic acid (19). Although the kinetics follows Figure 2, the resulting physical properties of the polyimide films are displayed in Figure 3. Three molecular weight divisions are plotted as a function of temperature versus qualitative physical properties, demonstrating the effect of the polyamic acid molecular weight on the polyimide during conversion. This effect can be rationalized knowing that the amount of chain scission is independent of molecular weight, resulting in a more dramatic effect on lower molecular weight polyamic acids. The lower molecular weight polyamic acid can be reduced to monomers, where these units may be thermally unstable and susceptible to oxidation. When this occurs, the adulterated monomers upset the stoichiometric balance resulting in low molecular weight polyimide. Higher molecular weight polyamic acids are less likely to be converted down to monomeric levels, and the oligomers will repolymerize to form medium or high molecular weight polyimide as stoichiometry is maintained.

An interesting reaction sequence, parallel to the two step synthesis of polyamides via the amide-salt process, has been outlined (7,58,59). Here, the diamine and tetracarboxylic acid are first mixed in water to form the salt precipitate, that is collected and dried. The resulting amine salt is placed in

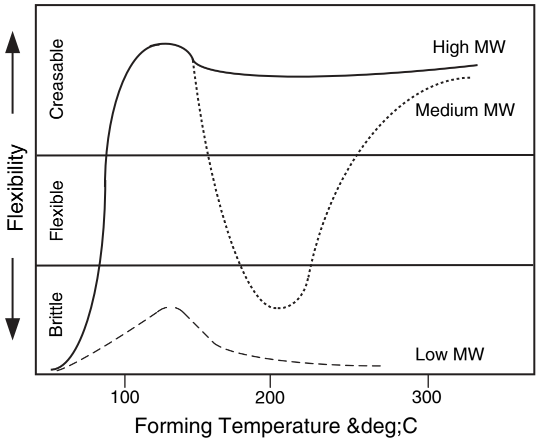


Fig. 3. Qualitative physical properties vs. molecular weight for thermally formed polyimide films (19).

water and heated under pressure to 130°C/1hr, then 180°C/2 hrs and cooled to ambient. The resulting polyimides have molecular weights and physical properties equivalent to those made by conventional two step methods.

Chemical imidization is not widely used because it employs additional reagents. However, it has the advantage of low temperature imidization and can be used to directly form fine polyimide molding powder (19, 60). A typical chemical imidization reaction employs a 20–30% solids polyamic acid in an amide solvent with a slight molar excess of acetic anhydride and a molar equivalent of a triamine (triethyl amine, pyridine or β-picoline) (61–64). The percent conversion for chemical imidization is a function of polyimide solubility. If the polymer crystallizes and/or precipitates from the reaction medium, imidization will be incomplete (19, 60). Those systems that remain soluble must undergo thermal treatment to convert any isoimide, and remove residual solvent. The mechanistic routes of chemical imidization are shown in Figure 4, and involve using a triamine to form the amine salt from acetic anhydride, *Step 1*, and the amine salt of the polyamic acid, *Step 2*. Next, the salt is replaced with the acetyl group (from the dianhydride salt) to form a mixed anhydride. The acetate group from the mixed anhydride group leaves as the amide nitrogen attacks the carboxylic acid carbonyl. The acetate group picks up the amide proton to form acetic acid resulting in the formation of the imide ring. If the polyamic acid is not in the proper conformation (i.e. the amide group may be rotated out of position) the carbonyl oxygen may attack the mixed anhydride to form the corresponding isoimide, *Step 3*. The isoimide is onverted to the imide thermally or by the presence of acetate ions that attack the ester carbonyl carbon, closely following the later stages of *Step 2*. The important step is the conversion of the polyamic acid's hydroxyl group into a better leaving group, the acetate (65, 66).

One system that takes advantage of both the chemical and thermal imidization is the gel casting of PMDA-ODA. This system starts as polyamic acid in NMP or DMAc to which is added β-picoline and acetic anhydride. This mixture starts to imidize and forms a gel as it is coated onto a rotating heated drum. The

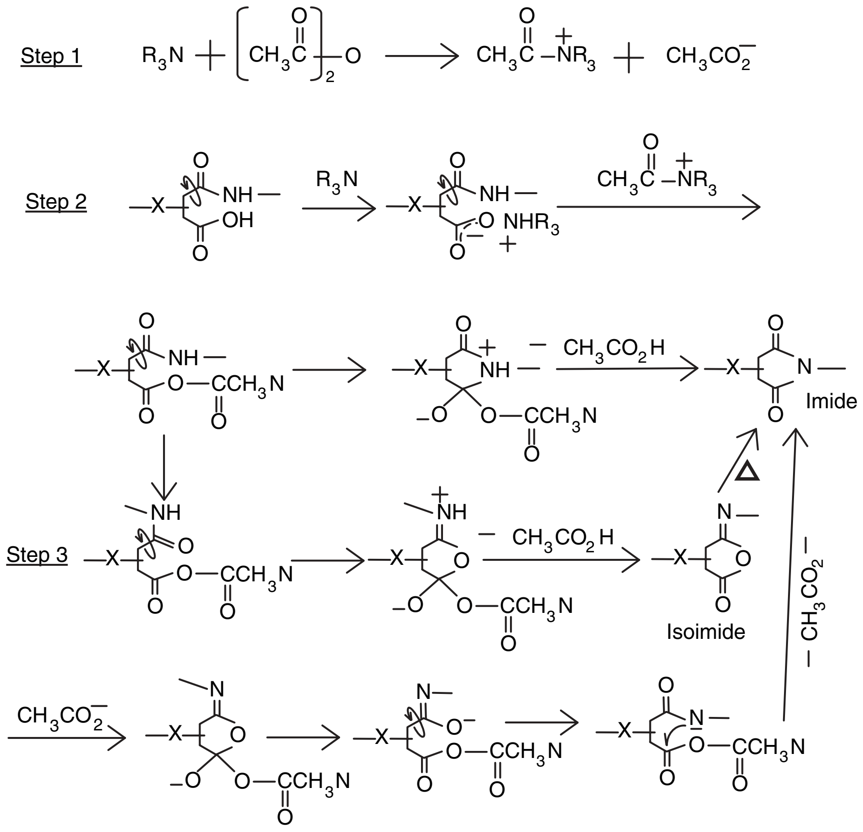


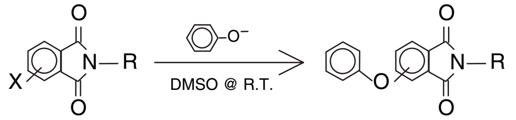
Fig. 4. Reaction diagram for chemical imidization via polyamic acid.

swollen gel film has mechanical integrity that allows it to be stripped off the drum and gripped by a tenter frame. Final conversion and solvent removal is achieved thermally (infrared and convection) while the film is undergoing mechanical orientation (67).

2.4. One Step Formation of Polyimides. Polyimides that are soluble in high boiling organic solvents can be directly converted from their corresponding monomers. This is done by mixing a diamine and a dianhydride into a solvent above 180°C. Typically, solvents such as m-cresol with catalytic isoquinoline, benzoic acid, nitrobenzene, or NMP are used depending on the polyimide formed (17,68–70). This system is useful for diamines and dianhydrides having low reactivity and those that are sterically hindered, such as perylenic dianhydrides (71,72). The conversion of monomer to polyimide proceeds rapidly with the intermediate polyamic acid being short lived to the point that it is virtually undetectable. The degree of imidization is nearly 100% (73–76).

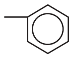
2.5. Synthesis of Polyimides Using Imide Containing Monomers. Two methods may be employed to form a polyimide when the imide ring is intact. The first method uses a high yield organic reaction where imide-containing monomers polymerize via a different mechanism (aromatic nucleophilic displacement). The second approach involves thermosetting imide oligomers.

Table 3.



Relative

Relativities of Substituted Phthalimides with Phenoxide in DMSO at Room Temperature[a]

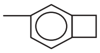
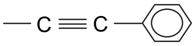
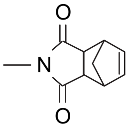
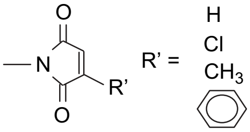
Position-X =	R = $^{-}CH_3$	R = 
3-Cl	1	–
3-F	4	20
3-NO_2	37	130
4-F	–	65
4-NO_2	170	520

[a] Ref. 82.

2.6. Polyimides via Aromatic Nucleophilic Displacement. Aromatic nucleophilic displacement is used in the synthesis of polyarylene ethers. Halogenated bisimides are polymerized with bisphenolates and activated A-B phthalimides to form polyetherimides (77–81). The reaction proceeds through the Meisenheimer-type transition lowering the activation energy of the displacement reaction. Table 3 shows the relative rates of displacement on substituted phthalimides with phenoxide, and it is worth noting that the displaced nitro group may affect the growing polyimide if not handled properly (77,82). A related synthetic method has been employed specifically for both bisphenols and halogenated diimides or the halogen containing A-B phenolated phthalimide monomers. Bisphenol or the N-phenol unit of the fluorinated phthalimide is converted to its corresponding trimethylsilated analogue. Polymerization of these silated monomers into polyimides are achieved in the melt at high temperature using cesium fluoride as a catalyst (83).

2.7. Polyimides via Addition Reactions. A second approach involves using maleimide terminated monomers (bismaleimides or BMIs) in equal molar ratios with a dinucleophile, such as a diamine, or a diene like dibenzocyclobutane (BCB) and substituted dicyclopentadienes to form the corresponding linear polyaspartimides via Michael-type addition or the polyimides via a Diels-Alder [4 + 2] cycloaddition (Table 4) (84–97). Linear polyimides can be synthesized directly from the A-B maleimidobenzocyclobutane monomers (96). These reactions proceed without volatile evolution, but undergo thermally initiated retrograde reactions that lead to change in physical properties, chemical crosslinking and aromatization of the cyclohexene ring (BCBs). Reactions involving BMIs with dicyclopentadieneones also proceed by a cycloaddition mechanism (94, 95). This has the same advantage inherent to all Diels-Alder reactions in that no volatiles are generated. However, with these pentadieneone dieneophiles, CO is eliminated forming a cyclohexadiene moiety. The cyclohexadiene can undergo further addition reactions or aromatize with the abstraction of two hydrogen atoms depending on the reaction conditions, and the added stability of any pendent substituents (94, 95). This type of chemistry can be used to create photosensitive polyimides

Table 4. **Chemical Groups Used for Functionalizing or Reacting with Polyimides (Sec. 2.7)**

Reactive group		Onset cure temp. (°C)	Comments on long term stability at 177°C
$—OC{\equiv}N$	cyanate	200–230	poor thermal stability
	benzocyclobutene	200–250	co-reacts with maleimide, poor long term stability
$—OCF{=}CF_2$	trifluorovinylether	250	small processing window, unknown thermal stability
$—C{\equiv}CH$	ethynyl	200	small processing window, unknown thermal stability
	phenylethynyl	320–370	excellent thermal stability
	nadimide	300–350	cyclopentadiene evolution, low toughness
	maleimide	200–230	poor thermal stability
	chloromaleimide	200–230	poor thermal stability
	methylmalimide	220–250	poor thermal stability
	phenylmaleimide	340–370	unknown thermal stability

for imaging. The last approach utilizes free radical polymerization of substituted maleimides to afford ethylenic-type imide polymers (98,99). Maleimide groups are copolymerized with unsaturated monomers such as styrene and other maleimides to afford copolyimides (100). Polymerization of these systems is typically carried out with AIBN in polar solvents such as THF (101). These types of polyimides can be used for a variety of applications from optical and photosensitive resins to structural materials, depending on the selection of the N-substituent (96,100).

Thermosetting systems involve the placement of reactive moieties with the polyimide, terminal, pendent, or blended as copolymers with the reactive imide monomer (Table 4). These systems contain maleimide, norbornene (nadic), vinyl and allylic, acetylenic, phenylethynyl, or other types of unsaturated groups that react to crosslink the polyimide (102–134). When bismaleimides are used alone or in excess with a difunctional (at least) nucleophilic monomer, the resulting system is thermosetting with chain extension (via Michael-type addition) occurring prior to the thermal crosslinking of the maleimide functionality (via Michael addition) (135–139). Although the crosslinking of the maleimide group is thermally initiated, it is catalyzed with both free radicals and bases (100,104,105). Typical synthesis involves 30% (or more) total solids diamine and two equivalents of maleic anhydride in acetone at ambient temperature. After the bismaleamic acid precipitates (several hours), triethyl amine is slowly added to the mixture until dissolution occurs (approximately 0.5 equivalents). Acetic anhydride (slightly over 1 equivalent) is added and the mixture is heated at reflux for several hours and the crude product is isolated by water precipitation. The intermediate maleamic acid is susceptible to isomerization during cyclodehydration resulting in the production of the less desirable acetanilide (95,104). Metal acetate catalysts have been known to increase the yields of BMI (140). However, it has been the author's experience that these catalysts tend to be difficult to remove and provide marginal benefit. Blends of BMIs with aromatic allyls and phenylpropenyl oligomers, such as a bisallylphenol, have been used as thermosetting systems that undergo complex reaction involving Ene addition followed by Diels-Alder addition, respectively (122,125,127,131–138,141–144).

The nadic group has been extensively explored for creating polyimide thermosetting resins including the “PMR” materials. These materials include the nadic endcapped LaRC 160, PMR-15, PMR-II, RP-46, Superimide 800 and others, and the nadic/amine terminated systems which includes AFR-700B. The nadic functionality is similar to the maleimide functionality in that it can undergo similar addition-type reactions and can form the maleimide upon rearrangement and release of cyclopentadiene. A study comparing the thermo-chemistry of these two moieties is described wherein time, temperature and free radical initiation were detailed (145). These nadic-terminated oligomers are formed from nadic anhydride (NA), a diamine and a dianhydride (119, 120, 146–153). These systems (like their aromatic counterparts) do not exhibit the same behavior as maleamic acid during imidization as structural conformation remains in place. Unfortunately, the nadimides generate cyclopentadiene at the elevated temperatures required to cure them. Hence, these systems must be cured under pressure to avoid volatilization of the cyclopentadiene that copolymerizes with itself, other nadic moieties and the resulting maleimide (154–156). In an attempt to create a high temperature thermosetting imide system that can be handled as a room temperature liquid, the PMR approach was developed (Polymerization of Monomeric Reactants). Here, the dianhydride and nadic anhydride are treated with molar equivalents of an aliphatic alcohol and allowed to form the liquid diacid-ester isomers. The diamine and the diacid-esters are then dissolved in methanol, and the liquid system is solution cast or coated onto a preform to create a prepreg that is dried and cured under pressure to form a composite part. The advantage of this system is that the monomers remain intact at or below room temperature (121,157–159). The molar ratios of the diacid-methylester of BTDA, 4,4′-methylenedianiline (MDA) and the acid-methylester of NA of 2.087:3.087:2 are used to make a 1500 g/mol imidized reactive oligomer referred to as PMR-15. There are several studies that characterize the reactive monomers, the cure chemistry and kinetics, cure cycles and the resulting thermo-mechanical stability of the various nadic systems made via the PMR approach (155–165). Acetylenic groups on polyimides are used to induce thermal crosslinking (166,167). The actual chemical structures developed during the acetylenic crosslinking can vary, as the reactivity of these groups is high enough to allow attack on chemical moieties other than acetylenic units (168). National Starch's Thermid IP-600® is an acetylene-terminated thermoset that has enhanced solubility, as it is an isoimide that thermally converts to imide when cured (169,170). The highest temperature thermosetting matrix resin/ structural adhesives were those based on phenylacetylene (phenylethynyl) (20, 126,171). NASA's PETI (Phenylethynyl-Terminated Imide) series are systems that cure at temperatures above 320°C (172–180).

2.8. Polyimides via Polymer Conversion. One method has already been introduced through the chemistry of isoimide synthesis and conversion. If the isoimide is desired directly, a polyamic acid is dissolved in a solvent system that facilitates removal of the by-product and a molar equivalent of dicyclohexylcarbodiimide "DCC" or similar cyclodehydrating agent. These isoimides are then converted by thermal conversion to the corresponding imide at elevated temperatures (181,182). Other methods involve transimidation and treatment of dianhydrides with diisocyanates. Transimidiation involves the exchange of one imide nitrogen functionality (as the amine) for another. This type of reaction is favored when the attacking amine is more basic than the amine that comprises the imide ring. Because of the lower reactivity of aromatic amines, in comparison to aliphatic amines, this type of reaction offers certain advantages. When the less basic 2-aminopyridine terminates imide oligomers, this amine can be readily exchanged for other aromatic diamines to form a high molecular weight polyimide through proper stoichiometric control (183–187). This scenario allows for the formation of otherwise infusible polyimides, via melt processing techniques, and also permits the incorporation of chemical moieties that are susceptible to hydrolysis via the polyamic acid route. Another conversion route involves the reaction of diisocyanates with dianhydrides to form the polyimide followed by elimination of CO_2 (188–195). There is not a general consensus on the mechanism of this reaction. Some researchers contend that the isocyanate reacts with water to form the amine or alcohol to form the urethanes that react with the dianhydride to form the polyimide (190). Others favor a seven membered ring formation that liberates CO_2 forming the imide ring (188). Metal salts have catalyzed these imide-forming reactions, and some have been polymerized in the melt (196,197).

3. Polyimide Structure-Property Relationships

3.1. Electronic Interactions. One of the features of polyimides is that the polyimide macromolecules interact with themselves and each other by either an electronic polarization or charge transfer mechanisms (198–200). The degree to which these mechanisms play a role depends on the electron affinity of the imide ring (deficiency) and the electron donating ability of the N-substituent (ionization potential) (201). The extent these electronic interactions effects neighboring polymer molecules influences the polyimide's color, glass transition temperature, crystallinity, mechanical properties and chemical resistance (202,203). It is apparent that the intrachain electronic polarization affords the yellow to dark orange color that arises in polyimides (202,203). The amount of chromophores present can be controlled to some extent by the selection of the cyclodehydration environment; choice of monomers, polymerization conditions and especially processing methods, and is not related to the presence of unconverted isoimide (202).

3.2. Structural Features. Generally, the bulk structure-property relationships that apply to most polymers apply to polyimides. The thermal transitions are influenced by the selection of monomers and processing techniques (204–207). Monomers that have kinks, offsets, swivel units, pendent substituents, aliphatic moieties and bulky units tend to lower the Tg, melt viscosity, crystallinity and increase solubility, as these units take up more free volume by introducing a more random structure than their symmetric counterparts (58,208–228). The proper selection of fluorinated monomers has produced nearly colorless soluble polyimides (201,202,206). One interesting and unique polyimide developed by NASA, LaRC-SI, does not use the standard approaches to develop solubility. This polyimide starts from a mixture of two dianhydrides, BPDA and ODPA and a diamine 3,4′-ODA to afford an amorphous high molecular weight polyimide that is soluble in common high boiling amide solvents (44,218,229). What is intriguing is that the two homopolymers, ODPA/3,4-ODA (LaRC-IA) and BPDA/3,4′-ODA, and the copolymer using ODPA/BPDA/4,4′-ODA are all insoluble and semicrystalline (218,229). There have been successful attempts of creating thermotropic polyimides. These liquid crystalline or “LC” polyimides rely on extended arylene ether-type diamines to create polyimide thermoplastics and blends, or thermosetting polyimides (230–232). The advantages of such systems are that they can be more easily melt processed, do to reduced thermotropic melt viscosity, and can undergo shear induced molecular orientation to gain additional property enhancements.

3.3. Thermal Stability. Aromatic polyimides are highly thermally stable because of their degree of aromaticity, ring structure and packing density, which are also a function of cure cycles (233–235). Typical decomposition points for polyimides, not subject to thermally initiated retro reactions, are above 450°C in air and above 500°C in nitrogen (236). Endcapping a polyimide with a stable monofunctional unit also enhances thermal stability by protecting chemically active chain ends that are subject to thermal and chemical instability (237,238). Treating polyimides at temperatures in excess of 500°C, under non-oxidizing conditions, results in a high yield ∼60%(w) of carbonous material. Analysis of the main volatile evolved from pyrolysis was the CO from the imide ring (239). These polyimide based carbon films and preforms have been derived for use as membranes and carbon/carbon structural components (240–245).

3.4. Enviromental Resistance. Polyimides are resistant to chemical attack, radiation and moisture. An exception is the PMDA containing polyimides that are hydrolyzed under basic conditions (246–248). The effect of degradation of one imide ring, in PMDA, changes the characteristics of the other ring via resonance through the common aromatic ring. This is also the case with monoaromatic diamines like pDA. However, most polyimides are highly resistant to caustics, acids, organic solvents, specialty fluids and salts, even at elevated temperatures (44,174,177,212).

3.5. Electrical Properties. The electrical properties and temperature range of polyimides have led to their widespread use as dielectrics, flexible substrates, electronic packaging and wire insulation for the electronics industry (249–257). An excellent review on some of the issues for reliability in electronic assemblies, from a materials standpoint, was published indicating moisture as one of the main mechanisms of electrical failure (258,259). Although the imide ring is polar and electron deficient, the two dipoles of the carbonyl groups oppose each other and the imide rings along the polyimide backbone also directionally oppose each other. This simulates the bulk effect of a non-polar polymer. Thus, polyimides make good dielectric materials when combining these properties with their high temperature and chemical stability (252,255–258,260–262). Typical dielectric constants range from below 3 to above 6, depending on structure, frequency, temperature and moisture absorption. As expected, fluorinated polyimides display dielectric constant typically 0.5 lower than the non-fluorinated polyimides, as the fluorine atom imparts low polarizability, water uptake and surface energy (263–268). Similar comparisons can be made from PTFE systems and their corresponding hydrocarbon analogues.

3.6. Mechanical Properties. The bulk mechanical properties of aromatic polyimides are among the highest for commercial plastics (269). The various processed forms of solid polyimides have excellent mechanical properties with elongations from 3 to 120%, tensile strengths and moduli 170–270 MPa and $>$3 GPa, respectively, over a wide range of temperatures from cryogenic to well above ambient. This is due to the interchain interactions of polyimides and their structural integrity imparted by their aromatic character, morphology and sub Tg transitions, that may impart additional toughness (170,270–273). Those polyimides that can undergo melt processing tend to make excellent hot melt adhesives.

4. Photoimageable Polyimides

Photoimageable polyimides are mainly used in microelectronic processing as soldier masks, protective coatings, and negative and positive photoresists for the selective etching and layering of complex circuitry on multilayered PCBs and silicon wafers (274). For such applications, these resins must have good substrate adhesion and wettability, a long storage life and high quantum yields upon exposure, undergo changes in solubility without swelling, and serve as a thermal protective coating, which is an inherent characteristic of polyimides. There are several ways (see Figure 5) in which polyimides have been used in applications where "photoimaging" is required to produce a pattern on a substrate (typically silicon, or other materials including polyimide itself) (275). The first method is reactive ion etching (RIE) (includes plasma etching) or photoablation. This method does not require a photosensitive material, only a mask that can withstand the reactive ion gas or photons and the material to be patterned, that is protected by the mask. In RIE, the reactive ions, generated by an RF field, attack the exposed polyimide to etch out the pattern of the mask. This process can be used with conventional polyimide film and requires few steps, but is not highly accurate and requires a hard (metal, silicon etc.) mask. The other methods involving the conventional polyimide, as a dielectric, require an additional photosensitive material as the overcoat. The method also

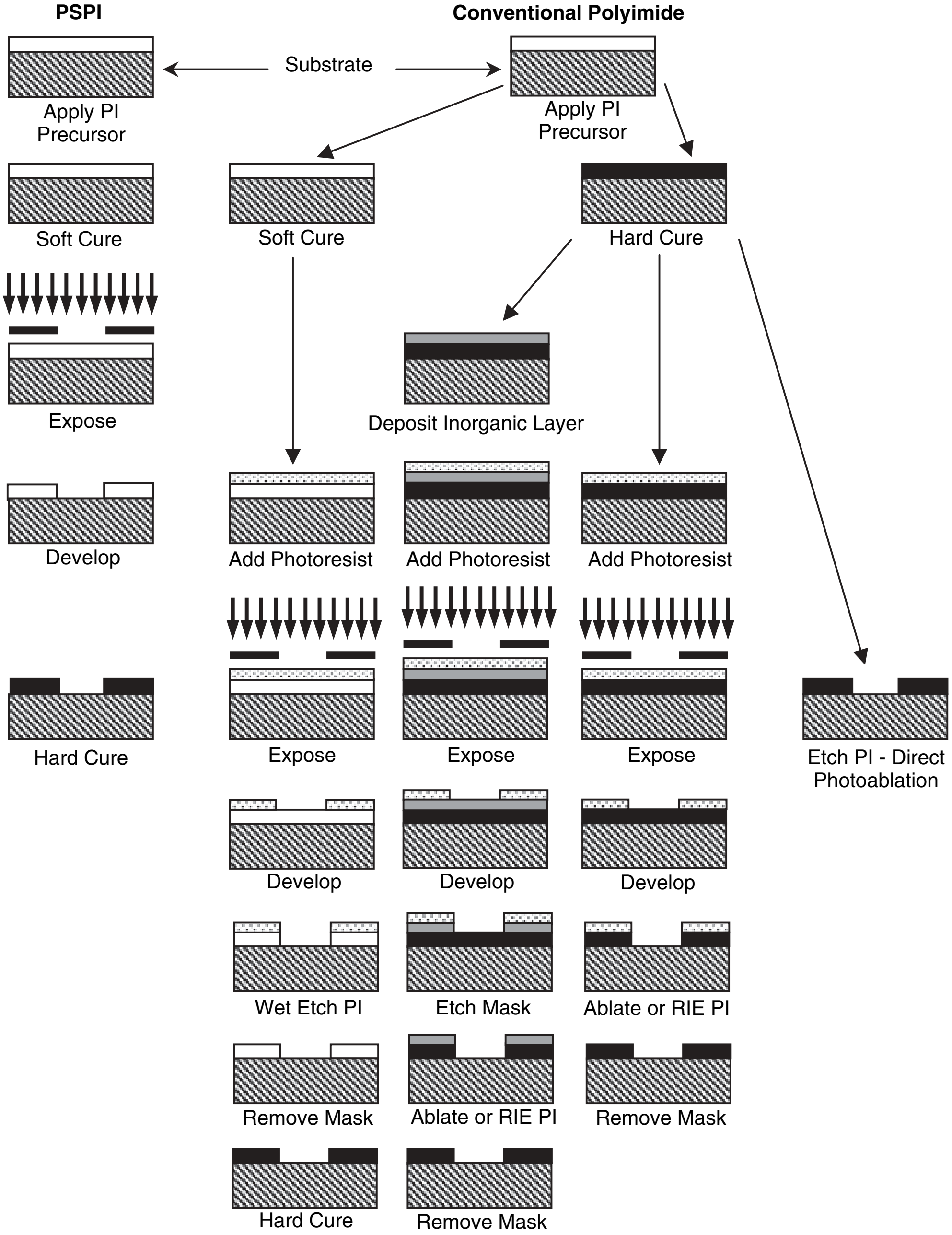


Fig. 5. Chart of Various Photoimaging Processes (259, p 744).

uses a mask, but higher degrees of accuracy are obtained as the photosensitive material's exposure is done with coherent short wavelength light. The combination of step reduction, increased accuracy and less complexity while maintaining good dielectric, mechanical and thermal properties have spurred the development of photosensitive polyimides, "PSPIs" used with these photoimaging methods (276,277).

4.1. Negative Photoresists. The two types of photimageable resists are positive and negative. The negative resist undergoes a reaction when exposed that typically decreases solubility, in comparison to the unexposed region, that remains in place during solvent development (a negative image is produced). Negative PSPIs are often used in their soluble polyamic acid with photosensitive units either attached to the polymer backbone, in conjugation with the carboxyl unit of the polyamic acid, or incorporated into the polyimide structure. Specific areas of the cast photosensitive film are exposed to light, thereby becoming insoluble through a crosslinking mechanism, and the masked portions (unexposed areas) are washed away with solvent. The remaining crosslinked (exposed area) is then baked to thermally cure the polyamic acid, releasing the crosslinked portion. Subsequent washing removes these crosslinked photocured regions. There are several approaches used to create negative PSPIs, with the more popular being those of the covalent, ionic and intrinsic types (278). The covalent type was one of the first and still widely used commercial approaches. A photosensitive unit is attached to the carboxyl group of the starting dianhydride prior to polymerization with a diamine (Figure 1, k_4 followed by k_3). The resulting sensitized polyamic acid is then exposed and the resulting sensitized ester unit photocrosslinks. The exposed film is then developed and baked (Figure 1, k_5). Such photosensitive units are of the acrylate or cinamyl variety (279,280). A system that uses a soluble fluorinated polyimide involves the chloromethylation of the aromatic ring on the arylether portion, followed by treatment with cinnamic acid to form the pendent photosensitive cinnamate group. This resulting PSPI was photocrosslinked, and the unexposed portion was washed away with solvent (281). The ionic type is similar to the covalent type with the pre-made polyamic acid sensitized by using a tertiary amine having a photoreactive group and a photoinitiator. The interaction of the tertiary amine and the polyamic acid hydroxyls form a photosensitized salt that is ionically bound to the polyamic acid (similar to Figure 4, *Step 2*). The ionic PSPI is then exposed, washed and baked to develop the image. The last type is the intrinsic PSPIs, meaning that they are photosensitive as made. These PSPIs are generally based on BTDA and orthoalkylated diamines. When these intrinsic systems are exposed to 365 nm wavelength, the hydrogen atoms of these pendent alkyls are abstracted through the excitation (C=O diradical formation) of the benzophenone radicals inducing crosslinking of the pendant methylene radicals. Overall resolution of negative PSPIs is controlled by several factors including film thickness, exposure wavelength and the selectivity of the developer, but the typical resolving limit that can be obtained is a 3:1 width to resist thickness ratio (274). These drawbacks of the negative PSPIs manifest themselves through pattern distortion, shrinkage, pinhole formation and thermal stability effects during wafer processing.

4.2. Positive Photoresists. The positive PSPIs undergo a chemical change in solubility on exposure, versus a molecular weight change. Typically, the masked positive PSPI is exposed to light and a pendent photosensitive unit is converted into a carboxylic acid or hydroxyl unit that allows the exposed portion polyimide to be removed under aqueous conditions (producing a positive image). The advantage at this point is that since the exposed and unexposed

PSPI are close in structure, there is reduced physical swelling on exposure, and the unexposed areas can be re-exposed with a different mask. Hence, these positive PSPIs lead to more accurate patterning and tighter line widths. Lastly, the positive PSPIs are baked to volatilize the pendant photosensitive units to afford the polyimide dielectric. Most of the chemistry of these positive resists use variations of the Wolff rearrangement of diazo systems (274). As an example, a polyimide with pendent hydroxyl groups was synthesized and blended with diazonaphthoquinone (DNQ). Here, the DNQ complexes with the pendant hydroxyl portion of the polyimide, decreasing the solubility of the polyimide towards aqueous base. Upon exposure, the DNQ undergoes the Wolff rearrangement, forming the indenecarboxylic acid and decomplexing from the polyimide. This results in increasing the solubility of the exposed polyimide mixture towards aqueous base solution (282,283). Other methods involve PSPIs made with acetal containing diamines. These are photo-catalytically depolymerized in the presence of *p*-toluenesulfonic acid, resulting in derivatives of benzaldehyde and hydroxy-phthalimides that are readily removable (284). PSPIs with pendent nitro-benzylester groups can be photo-degraded to the corresponding aryl-acid functionality to enhance the resulting converted polyimides solubility in caustic solutions, with the additional advantage of subsequent thermal removal of the nitro-benzylester group form the unexposed portion (285). Most of these post-thermally developed PSPIs, negative and positive, have mechanical properties close to that of standard polyimide film, from which they are derived, thus demonstrating excellent planarity (surface flatness), high voltage breakdown resistance and low dielectric constants.

5. Polyimide Applications

Polyimides are manufactured in a variety of forms, finding utility ranging from electronics and medical to structural and adhesive applications. The major forms of polyimide are films, molded and extruded stock, fiber reinforced adhesive tape, varnish, foam and composite prepreg.

5.1. Polyimide Film. One of the more prevalent forms of polyimides are films. The most popular films are Dupont's Kapton®, Ube Industries Upilex® and GE's Ultem® and Kanekafuji's Apical® to name a few. In film form, some of these materials do not display a Tg, have good radiation resistance and are used as bagging materials for composites, belts, insulative wire wrapping and flexible circuits. They are coated with acrylics and silicones to make pressure sensitive tape (286). Polyimide film is also adhesively to bonded to metal foil (copper) to one or both sides, and sold to PCB manufactures for flexible cabling and circuits (examples include DuPont's Pyralux® and clad derived from Kaneka's Apical® series of PI films). Metal is also vapor deposited onto polyimide film for applications requiring thin copper or other metals (less than 0.5 oz/12 µm) where the additional adhesive is undesirable. Since these films and clads serve as dielectric materials, they are tested under IPC TM-650 tests and display breakdown voltages above 200 V/µm (5 kV/mil) and 1 MHz dissipation factors of 3.2 on average (202). Several methods to create metallic coatings in-situ involves the introduction of silver organic salts (complexed silver(I) acetates) or other metallic complexes into the polyamic acid. Through thermal imidization, that may be photo-assisted, the silver metal is reduced and migrates to the surface to form a reflective coating (287–291). Another method involves chemically etching the polyimide surface forming the carboxylic acid groups and exchanging these protons with silver ions followed by UV radiation (292). This has the advantage of not depositing metal ions throughout the film thickness. The latest trends in polyimide dielectrics is the introduction of nanotechnology in order to improve the insulative properties or electrical conductively. A nanoporous polyimide film was developed by blending the amic acid with PEO and POSS, followed by thermal imidization and thermal oxidation, resulting in a nanoporous silicon oxide polyimide film with a reduction in the dielectric constant of 1 (293). A 3-D flex circuit was created by embedding nanowires into polyimide film by heavy ion implantation followed by surface etching and gold deposition to create conductive patches. The goal was to develop Z-axis conduction for flex circuitry and magnetic sensing applications (294).

5.2. Polyimide Coated Wire. For years, the electrical and aerospace industry has used polyimides as high performance wire insulation. These coatings are used in combination with other materials and may either be biaxially wrapped onto the wire, solution coated and dried in multiple passes to form a varnish, or directly extruded over the wire. The polyimide insulation must survive tight radial bends, chaffing and electrically induced oxidation and carbon tracking (295–298). Since polyimides possess high dielectric strength, thermal stability, radiation resistance and are self extinguishing, they are employed in both air and spacecraft (299–303). The low earth orbit conditions are especially devastating for organic polymers due to the presence of atomic oxygen and UV radiation (304–306). This has lead to the incorporation of silicone and phosphine oxide units in the polyimide that resists the atomic oxygen degradation. The NASA LaRC-TOR series polyimides, that contain phosphine oxide units in the backbone, have been one of the leading polyimides for low earth orbit satellite and vehicle applications (307–310).

5.3. Polyimide Membranes, Tubes, Fibers and Foams. The fabrication of microporous membranes, thin walled tubes, fibers and films is done by solution casting or dry-jet spinning followed by heat treatment. These asymmetric flat or hollow fiber membranes are used the selective separation of gas and liquid mixtures. The main parameters for polymeric-based membrane material selection are the free volume, the molecular distance, which relates to porosity, the shape of the molecules, the burst pressure, temperature range and of course, the mixtures that require separation. Here, polyimides, with bulky substituents, display the highest fluxes and selectivity when compared to other glassy polymeric materials including polyphenylene oxides (311). The asymmetry is introduced by selective solution blending of solvent/non-solvent mixtures to generate a porous gradient, during polymer precipitation, across the membrane wall. This is followed by thermal evaporation techniques to set the final microstructure (312–319). In some cases, the surface wettability is improved by treating the polyimide surface with acids to increase the hydrophilicity without sacrificing thermal stability, which is especially important for fuel cells (320,321). Lastly, the one surface may consist of porous ceramic coating to facilitate ion transport (322). Thin walled polyimide tubes created from

PMDA and BPDA-ODA polyimides cannot be made via melt processing and are created by successive layering and drying to build up thickness on or inside a fused silica tube (323,324) These polyimide coated tubes find use as GC columns for chemical separation and as catheter medical tubing (325–327). Continuous fibers, solution spun and dried from polyamic acid or as the polyimide, present a challenge as the solvent, cyclodehydration and shrinkage problems associated with curing the fiber result in a technical challenge. Although the properties of these fibers are excellent when the proper draw ratio is used, they have not achieved a high performance niche market able to economically compete with polyesters or polyaramides (328–331).

The extensive processing methodology and physical characteristics make polyimides excellent resins for the design of foamed preforms. The thermal range, density variance and char characteristics make polyimide foams choice candidates for structural insulation, flexible gaskets, acoustical insulation and thermal protection for aerospace and naval vessels (332). These foams can be created from momomer solutions, amic acid gel or powder with blowing agents and solvent complexation. These components may undergo volatile release on thermal conversion to help develop and control the resulting cellular structure (333–338). These methods are used when creating open cell polyimide foams of varying density. The final cell size and type depends on both the thermal cycle and the diffusion rate of the agent out of the particle cell (339). One of the leading candidate polyimide foams for cryo-tankage insulation are NASA's TEEK series that have applications for the next generation of aerospace vehicles (340–342).

5.4. Melt Processable Polyimides. Polyimides that display a Tg and Tm well below their decomposition or thermosetting temperatures are candidates for melt processing techniques that include extrusion, injection and compression molding. Several other factors play into the selection of melt processable polyimides and include melt viscosity, work time or pot life at temperature and the ability to carry fillers or blends. Melt viscosity is crucial as it directly relates to molecular weight, affecting the processing temperature (193, 343–345). The higher the molecular weight, the higher the temperature and pressure needed to create the part. As the polymer's molecular weight increases, the mechanical properties increase until a critical molecular weight is obtained, where the melt viscosity increases while the mechanical properties start to level out. This "knee" or bend in the mechanical and physical properties versus molecular weight curve is where any further increase in molecular weight increases the complexity of the melt forming without a significant improvement in the overall properties of the neat resin (343–345). The influence of molecular weight and its relationship to melt viscosity are affected by the structure of the polyimide in a fashion similar to the basic structure property relationships discussed earlier. Several resin systems developed by GE, NASA Langley, Furon, Mitsui and others have found utility as thermoplastic molding resins. The Tg for these thermoplastic polyimides are in the range of 210°C to 270°C and are processed 50°C to 150°C above their glass transition temperature (343, 344). The molecular weights of these resins range from several thousand to above 30,000 g/mol. These systems display excellent fracture toughness and high modulus and have been extruded, compression molded, machined and polished neat, or filled with graphite, PTFE, metal and ceramic powders. These thermoplastic polyimides are sold as rod, sheet and film stock or as final stock parts and composites (245, 346–351).

Thermosetting polyimides solve the molecular weight effect on melt viscosity, but add the additional problems associated with curing exotherms and time/temperature limited processing windows. Thus, a wide processing window from the melt flow of the monomer(s) to the onset cure temperature should be selected. The melt processable thermosetting systems are typically BMIs, PMRs or BCB-maleimides, and these can blended with chopped fibers or other fillers, ground or extruded and pelletized for moldings (352–358). These imide oligomers are then cured into high performance PCB substrates and composite forms. Recently, NASA Langley has developed and commercialized several PETI based low viscosity thermosetting resins, PETI-298 and 330, that can be injection molded or resin infused into carbon fiber performs and then crosslinked at elevated temperatures (359).

5.5. Direct Formed Polyimides. There are several polyimides that do not undergo melt flow, but are directly formed into parts requiring performance under extremely harsh conditions (360, 361). These direct formed polyimides include DuPont's Vespel (includes the SP product line), Ube's Upimol-S and Imitec's I-903 and I-772. These polyimides undergo a forming process similar to that of ceramic sintering. The starting fine particle polyimide powder is either hot isostatically pressed (HIPed) or ram extruded and hot formed to generate a polyimide stock shape that is machined to size, with a density in the range of 1.4–1.5 g/cc for the neat system (362). These polyimide powders or films have also been blended/impregnated with graphite, PTFE and boron nitride for dry lubrication where tribology and abrasion issues are important (363,364). These parts have very low CTE and do not smear under load at elevated temperatures, making them excellent choices for high temperature PV (pressure-velocity) requirements (365–368). These molded parts have found utility in rotating equipment, silicon wafer and chip processing, machine tooling and chemical and material processing.

5.6. Polyimide Matrix Composites and Adhesives. Polyimides display properties that make the resulting advanced composites excellent choices as primary structural members for aerospace applications (369,370). The fibers in the composite are the load carrying members and the resin serves to transfer the load to the fibers and hold them in place. The composite is only as good as the resin (371). Thus, the selected matrix resin must have excellent thermal, chemical and mechanical toughness, high compressive strength and adhesive properties. One of the key elements in creating a strong composite is the wetting out of the fibers with the proper amount of resin. This is achieved by two methods, dry and wet (or solution) prepregging (372). The dry coating method may consist of coating the fibers with fine polyimide powder and melt shearing the powder to form a film about the fibers (373,374). Another dry process involves melt infusing a polyimide film into a fiber matrix affording prepreg tape. Solution prepregging involves the coating of the fibers with a solution containing the polymer or reactive monomers and removing the solvent at a later stage to form the prepreg tape. The resulting prepreg should display tack and drape i.e., tack to allow it to remain in place prior to and during consolidation, and drape to allow it to contour to the tooling surface. These prepregs are then cut into the desired shapes, stacked and laminated together on a tool in a hot press or autoclave to form the composite part. In order to achieve excellent consolidation, these polyimide laminates must undergo melt flow and adhere (350). Hence, the polyimides must display high adhesive strength under a variety of conditions (375–378). Initial criteria for screening the hot melt aerospace polyimides is the Titanium-Titanium or Aluminum-Aluminum Lap Shear test (ASTM D-1002), and for the electronic industry, the T-peel and 180° peel tests are used (ASTM D-1976 & D-3330). Titanium lap shear strengths for polyimide adhesives range from 2000 psi to over 8000 psi under ambient conditions. It is worth noting that surface preparation plays a key role in determining the adhesive strength of the resin system. The polyimide resin systems that have been used for aerospace composite programs include BMIs, PMR-15, DuPont's Avimide® series (based on the PMR approach) and NASA's PETI-5 (developed under the HSR program) that exceeds the performance criteria for the High Speed Civil Transport as a structural adhesive and matrix resin for this advanced composites program (350,379–381).

6. Conclusion

Polyimides are a class of high performance, highly versatile resins that can be tailored for application through the use of chemistry, processing, molecular weight control and reaction conditions. Polyimides display excellent thermal, mechanical and physical properties that place them in a general use category as material systems that can compete with other structural materials, mechanical fasteners, higher voltage connectors and chemically resistant parts. As the requirements for lighter weight, broader temperature performance, increased strength, durability and inertness continue to drive technology, polyimides will play an increasing role in the innovations of the future.

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