

Synthesis, Characterization, and Properties of Fully Aliphatic Polyimides and Their Derivatives for Microelectronics and Optoelectronics Applications

Anu Stella Mathews, Il Kim, and Chang-Sik Ha*

Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

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Abstract: Polyimides are one of the most important classes of polymers used in the microelectronics and photoelectronics industries. Because of their high thermal stability, chemical resistance, and good mechanical and electric properties, polyimides are often applied in photoresists, passivation and dielectric films, soft print circuit boards, and alignment films within displays. Recently, fully aliphatic and alicyclic polyimides have found applications as optoelectronics and inter layer dielectric materials, due to their good transparencies and low dielectric constants (ϵ). The low molecular density, polarity and rare probability of forming inter- or intra-molecular charge transfers, resulting in lowering of the dielectric constant and high transparency, are the most striking characteristics of aliphatic polyimide. However, the ultimate end use of polyimides derived from aliphatic monomers is in their targeted applications that need less stringent thermal requirements. Much research effort has been exerted in the development of aliphatic polyimide with increased thermal and mechanical stabilities, while maintaining their transparencies and low dielectric constants, by the incorporation of rigid moieties. In this article, the recent research process in synthesizing fully aliphatic polyimides, with improved dimensional stability, high transparency and low ϵ values, as well as the characterizations and future scope for their application in micro electric and photo-electronic industries, is reviewed.

Keywords: aliphatic polyimide, polyimidosiloxane, dielectric constant, electro-optic applications, charge transfer complex.

Introduction

Polyimides (PI) possess excellent thermal, mechanical, and electrical properties and thus have found immense applications in many technologies ranging from microelectronics to high temperature matrices and adhesives to gas separation membranes.¹⁻²⁰ The first synthesis of a polyimide from 4-aminophthalic acid was performed by Bogert and Renshaw in 1908.²¹ However, a high-molecular weight aromatic polyimide was first synthesized in 1955 by Edward and Robinson.²² Poly(4,4'-oxydiphenylene pyromellitimide) (PMDA-ODA PI) widely known as Kapton[®] which can remain stable in a wide range of temperatures, from -269 to +400 °C was first commercialized in early 1960s.²³ Kapton[®] film is used in, among other things, flexible printed circuits (flexible electronics) and spacesuits. Kapton[®] insulated wiring has been widely used in civil and military avionics (electrical wiring for aircraft) because of its very light weight compared to other insulator types as well as good insulating and temperature characteristics. The NASA Jet Propulsion Laboratory has considered Kapton[®] as a good plastic support for solar

sails because of its long duration in the space environment.²⁴ Kapton[®] is also used to monitor the flux on x-ray sources. A number of PIs have been synthesized and investigated extensively in aspects of structure and property relationships and applications after the success with Kapton[®].²⁵⁻³⁷ PIs are known to be thermally stable due to its heterocyclic imide rings on the backbone, and the thermal stability is further significantly improved by incorporating aromatic rings on the backbone and/or side groups. In addition to such high thermal stability, the nature of the chemical structure consisting rigid imide and aromatic rings always provides excellent mechanical and dielectric properties as well as high chemical resistance. Beyond these advantageous properties, a variety of functionalities (for examples, photo reactivity, molecular recognition ability, nonlinear optical responsibility, light emit ability, and so on) can be added into the backbone and/or side groups of PIs, depending on their demands in applications.³⁸⁻⁴² Due to these advantageous properties as well as the functionalities, PIs have found diverse applications in the microelectronics, flat panel display, aerospace, and chemical and environmental industries as flexible circuitry carriers, stress buffers, inter dielectric layers, passivation layers, liquid crystal alignment layers, varnishing resins,

*Corresponding Author. E-mail: csha@pusan.ac.kr

fibers, matrix materials, and gas and chemical separation membranes.⁴³⁻⁵²

Classification

According to the monomers from which PIs are derived, they can be broadly classified as fully aromatic PIs, semi aromatic PIs and fully aliphatic PIs (Figure 1). Aromatic ones are derived from an aromatic dianhydride and diamine. Semi aromatic ones contain any one of the monomer aromatic i.e. either a dianhydride or a diamine is aromatic, and the other part will be aliphatic. Finally the third category compiles of the polymers formed as a result of the combination of aliphatic dianhydride and diamine.

Aromatic PIs are typical of most commercial PIs, such as Ultem® from GE. and DuPont's Kapton®, and are therefore the PIs we will be spending most of our time on. These polymers have such incredible mechanical and thermal properties that they are used in place of metals and glass in many high performance applications in the electronics, automotive, and even the aerospace industries. These properties come from strong intermolecular forces between the polymer chains. A polymer which contains a charge transfer complex consists of two different types of monomers, a donor and an acceptor (Figure 2). The donor has plenty of electrons to go around because of its nitrogen groups and the acceptor with their carbonyl group draws away its electron

density. So the donor lends some of its electrons to the acceptor, holding them tightly together. Thus the polymer chains will stack together like strips of paper, with donors and acceptors paired up due to the formation of charge transfer complex between adjacent units in the polymer chain as shown in Figure 2(b). This charge transfer complex holds the chains together very tightly, not allowing them to move around very much. When things can't move around on the molecular level, they can't move around in the whole material. This is why PIs are so strong. The charge transfer complex is so strong; it sometimes becomes necessary to make the polymer a little softer so it is able to be processed. Aromatic PIs synthesized from only aromatic monomers are often insoluble in their fully imidized form thus having a low processibility. In addition, as most of the aromatic PIs absorb visible light intensely, they cannot be used in areas where colorlessness is an important requirement. It is well known that the origin of coloration in aromatic PIs is caused by the inter and intra molecular charge transfer (CT) interactions between the five membered ring of the imide group and the aromatic ring as explained above in Figure 2. High dielectric constant also arising from these interactions is also a demerit of aromatic PIs. Despite of its all excellent properties, low processibility, high dielectric constant and light or dark yellow coloration hinders its successful application in optoelectric materials and high-speed multilayer printed wiring boards. Efforts to suppress the CT interactions have

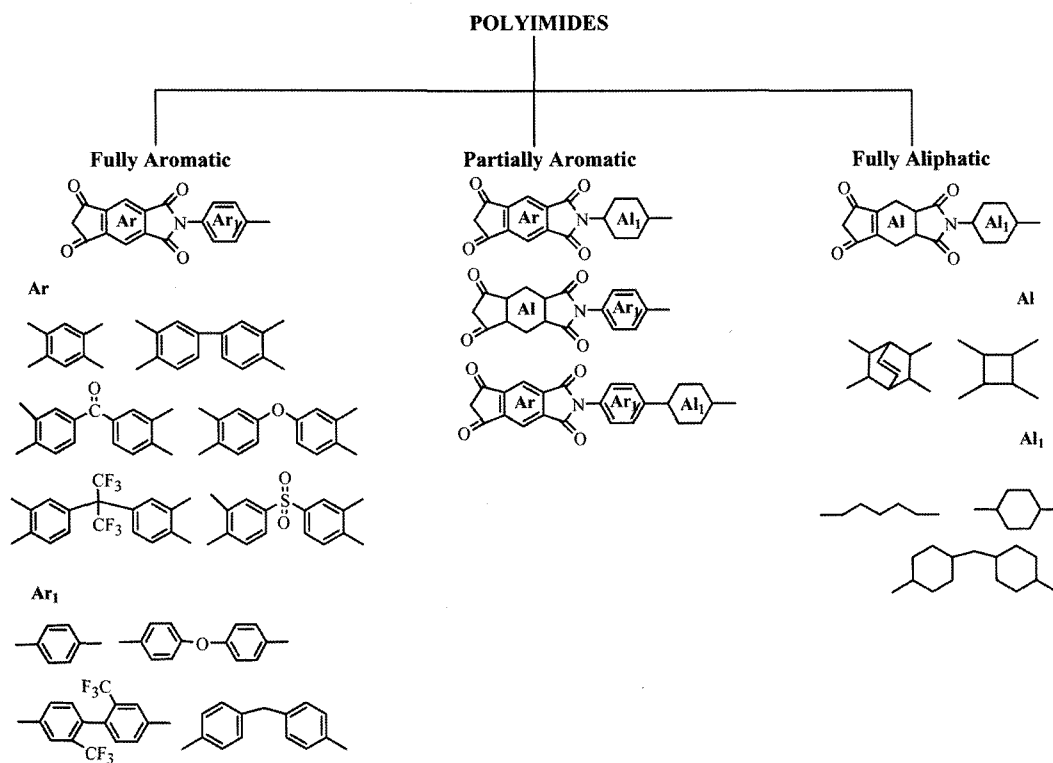


Figure 1. Classification of polyimides into 3 broad categories depending upon the chemical structure of the backbone.

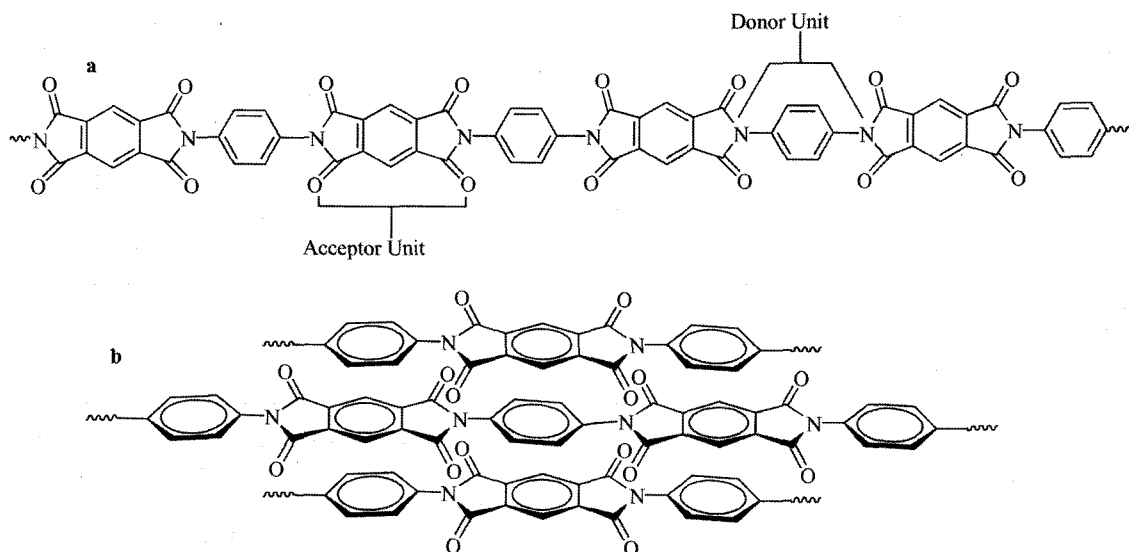


Figure 2. The donor acceptor system prevailing in PIs and the resulting interchain locking. (a) Nitrogen atoms having a higher electron density than the carbonyl groups lend it to the acceptor while carbonyl groups draw electron density away from the acceptor unit. (b) Interchain interlocking of PI backbones. Polyimides may stack like this allowing the carbonyl of the acceptor on one chain to interact with the nitrogens of the donor on the adjacent chains.⁵³

included the use of siloxane,⁵⁴ sulfonyl,⁵⁵ fluorinated,⁵⁶ and aliphatic⁵⁷ moieties. Among these, aliphatic structures display a lower dielectric constant and higher transparencies which result from their lower molecular density and polarity and low probability of undergoing inter or intra molecular charge transfer. Thus incorporation of aliphatic units to enhance the desired properties was applied widely.

Aliphatic Polyimides

Aliphatic polyimides (APIs) excel aromatic ones in high transparency, higher processibility resulting from higher solubilities and lower dielectric constant. The paper by Toshihiko Matsumoto⁵⁸ compares the properties of semi-aromatic and aliphatic PIs in details. In that study tetracarboxylic dianhydrides bearing a poly alicyclic structure, bicycle [2.2.1]-heptane-2,3:5,6-tetra carboxylic 2,3,5,6-dianhydride (BHDA), Bicycle [2.2.2]-octane-2,3,5,6-tetra carboxylic 2,3:5,6-dianhydrides (BODA), (4arH, 8acH) decahydro-1t, 4t:5c, 8c-dimethano naphthalene-2,3,6,7-tetra carboxylic 2,3:6,7-dianhydrides (DNDA), and bicycle [2.2.1] heptane-2-exo, 3-exo, 5-exo-tri carboxyl-5-endo-acetic 2,3:5,5-dianhydride (BSDA) were synthesized and polycondensated with aromatic diamines or a polyalicyclic diamine, bis(aminomethyl)bicycle [2.2.1] heptane (BBH), in DMAc, NMP, DMI or HMPA at room temperature or 60-105 °C under nitrogen. The polymerization solutions gave the flexible and free-standing PI films after being cast on glass plates and then cured. The films were soluble in aprotic polar solvents such as DMAc and NMP at room temperature. Among the films, some dissolved in CHCl₃ or 1,4-dioxane. The PIs showed

thermal stability and the 5% weight loss temperatures in N₂ were over 450 °C. The PI films exhibited T_g values in the range of 280-400 °C. The cutoff wavelengths of the non-aromatic PIs such as PI (DNDAx-BBH) and PI (BHDAx-BBH) were shorter than 235 nm, and around 290-330 nm for the semi-aromatic PIs. The transparencies in the visible region (400-780 nm) were over 85%. The flexible PI films possessed an average refractive index range of 1.522-1.617, and the optical anisotropies were 0.000-0.017. The dielectric constant ϵ values that were estimated from the refractive indices according to the modified Maxwell's equation were 2.55-2.87. Another study on fully APIs⁵⁹ describes the preparation of APIs by poly(addition-condensation) of the alicyclic dianhydride bicycle [2.2.2] octane-2,3:5,6-tetracarboxylic 2,3:5, 6-dianhydride with the aliphatic diamine 5-amino-1,3,3-trimethylcyclo-hexanemethylamine, the mixture of 2,5- and 2,6-bis(aminomethyl)bicycle [2.2.1] heptane or 1,4-cyclohexanebis(methylamine) in *m*-cresol at high temperature. The polymerization proceeded smoothly at 200 °C and produced APIs with inherent viscosities up to 0.48 dL g⁻¹. These studies showed that fully APIs processed high transparency and solubility and low dielectric constant than that of semi-aromatic PIs. Nevertheless, PIs derived from aliphatic monomers are most suitable for applications that have less stringent thermal requirements. The higher flexibility and low rigidity, resulting in low bond strength, of their backbone due to the aliphatic moieties makes their thermal and dimensional properties inferior to that of aromatic ones.

It is well known that rigid-rod structures reduce the coefficient of thermal expansion (CTE) of PIs.⁶⁰ Adamantane (tricy-

cle [3.3.3.1.1.^{3,7}] decane), a rigid alicyclic compound composed of three cyclohexane rings in chair conformations,⁶¹ is the most salutary alicyclic candidate for incorporation into APIs, to enhance their thermal stability without sacrificing their high transparency, solubility and low dielectric constants.⁶² Adamantane's diamond-like cage structure is relatively insensitive to degradation reactions caused by nucleophilic, electrophilic, or elimination reactions. The presence of pendent adamantane groups often causes dramatic increases in the glass transition temperatures and solubility of polymers without sacrificing their thermal stability. The bulkiness of the adamantane units tends to inhibit the packing of polymer chains; this process ultimately decreases their crystallinity and increases their solubility.⁶³ Chern *et al.*^{62,64,65} and Watanabe *et al.*⁶⁶⁻⁶⁸ reported the synthesis relatively thermally stable PIs semi-aromatic PIs containing adamantane and biadamantane moieties. Seino *et al.*^{59,69} and Mathews *et al.*^{70,71} have reported the synthesis and characterization of a series of fully APIs with good thermal and dimensional stabilities.

Oishi *et al.*⁷² reported fully alicyclic PIs containing fluorine groups while Mathews *et al.*⁷¹ focused on the synthesis of siloxane containing APIs. Fluorination provides unique properties to PIs, such as reduction of dielectric constants and refractive indices, improvement of the transparency in the visible and near IR region, lowering of glass transition temperature, change of reactivity of compounds (in particular, that of diamine), increase in free volume, decrease of water absorption, rise in thermal decomposition temperature, increases solubility, gas permeability, radiation-durability and thermal expansion coefficients.⁷³⁻⁷⁵ On the other hand, increasing importance of PIs for gas-separation, micro-electronics, and optoelectronics applications have paved the way for the introduction of silicon moieties into the backbone of PIs, promoting significant increase in permeability, perm-selectivity, and adhesive ability.⁷⁶⁻⁷⁹ Thus, more recently, silicon containing aromatic polymers has attracted much scientific and technological interest because of their superior permeability and adhesive ability between substrates and PIs together with low dielectric constant.⁸⁰⁻⁸² Polyimide-siloxanes (PISiO), the segmented copolymers containing siloxane segment along the intractable backbone chain of aromatic PIs, maintain some of the excellent properties of PIs, e.g., high thermal stability and mechanical strength and some of the desirable properties of siloxanes, such as ductility and adhesion as well as low moisture permeability. Superior solubility even in organic solvents with low boiling point meliorate the processibility of fully imidized PISiOs by replacing a prolonged polymer curing step at elevated temperature with a baking procedure at a lower one, while maintaining the thermal and mechanical stability.^{83,84} These excellent properties imparted by fluorine and siloxane group motivated researchers to incorporate them to aliphatic backbones and compare the variations they bring

to the basic traits of these PIs.

Monomers for Fully Aliphatic Polyimides

The structures of aliphatic monomers commonly used for synthesis of APIs in previous studies are given in Figure 3.^{58,59,66-72} Among them dianhydrides **A**, **B** and all diamines except **12** and **13** are commercially available. Literature 85-88 describes the synthesis of dianhydrides **D**, **E**, and **F** and Sieno *et al.* gives the synthesis scheme of dianhydride **C**.⁸⁵⁻⁸⁸ Dianhydride **A** and **B** has proved to impart excellent thermal and optical properties to PIs. The demerit of **B** is the presence of a double bond which can impart polarity decreasing transparency. So the compound **B** is oxidized to **C** to get more utile results. Dianhydrides **F** and **G** are asymmetric and thus can provide more free volume and lessen interchain interactions. Mathews *et al.* utilizes diamines **1-4** to study the impact of long chain and highly flexible backbones in PIs. **5** and **6** attracts the attention due to the formation of ortho and para linkage of imide group. Diamine **7** is non-coplanar so can decrease the dielectric constant more. The comparison of properties with the presence of methyl groups is obtained with diamines **9**, **10**, and **11**. Literatures 64, 67 and 69-71 report the synthesis of adamantane containing diamines **12** and **13**.^{64,67,69-71} As previously stated adamantane moieties are expected to impart many excellent properties to fully APIs. Structures of the diamines used to synthesis APIs containing fluorine and siloxane groups are shown as **14-17** in Scheme I. The influence of fluorine and siloxane moieties upon fully APIs can be drawn using those diamines.

Fully APIs can be built using single dianhydride and diamine groups which can be termed as homo-polyimides and also they can be derived from more than one dianhydride and diamine monomer combined together in definite molar ratios. As mentioned earlier aliphatic polycyclic PIs would be expected to have low dielectric constant and high thermal and dimensional stability but however, matching the coefficient thermal expansion (CTE) of the polymer with the substrate is difficult. Seino *et al.* and Mathews *et al.* reports the homopolyimides made of the rigid adamantane backbones produced are very brittle films due to the mismatching of the CTE of the APIs with that of substrate. A number of approaches have been reported to rectify this problem, such as utilizing a combination of rigid and flexible alicyclic monomers.⁸⁹ Copolymerization of rigid monomers with flexible ones has been used to control the thermal and mechanical properties of PI to meet specific processing and property requirements. Thus the highly brittle films arising from the highly rigid alicyclic homopolyimides can be replaced with good films of copolyimides. The copolyimides with alicyclic diamines and adamantane diamines and flexible alicyclic diamines with adamantane are reported in the above stated previous literatures.

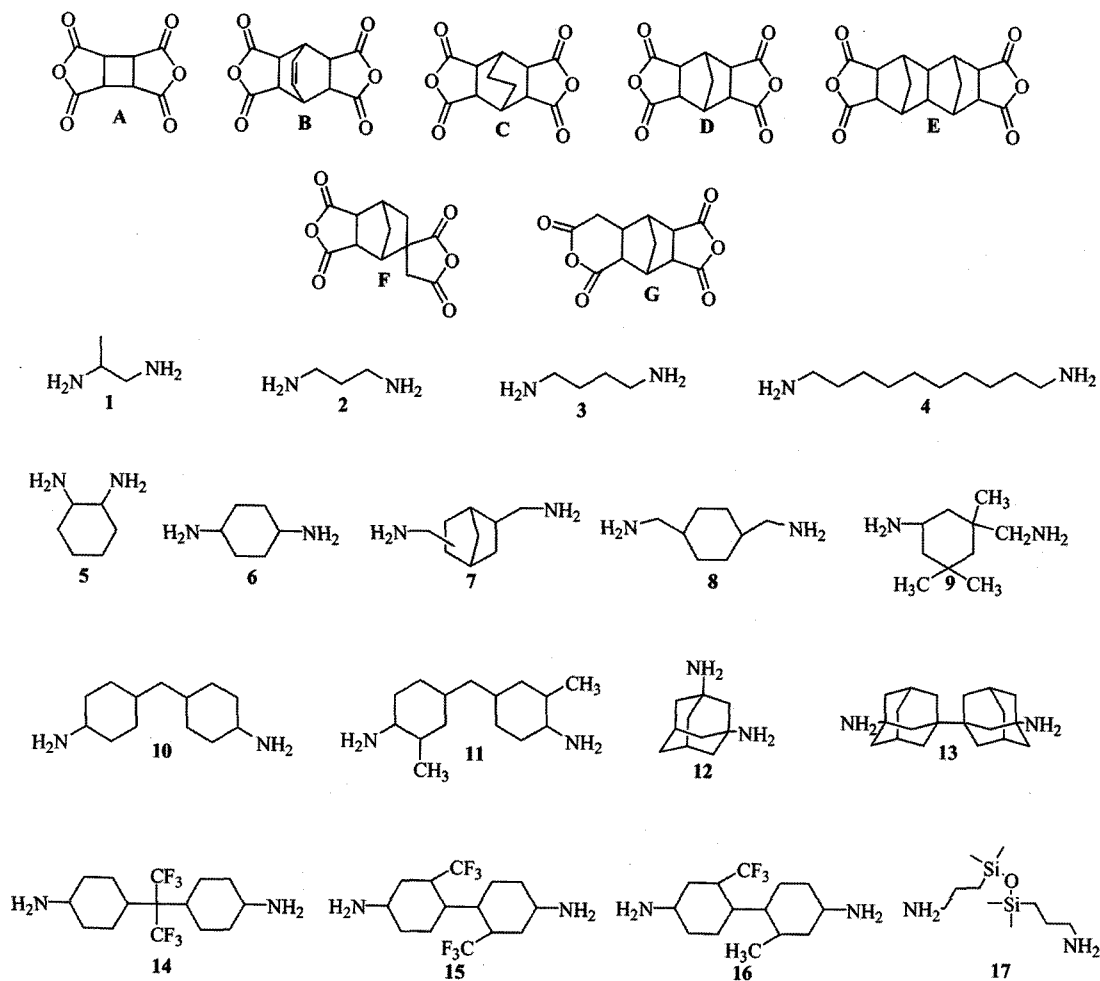
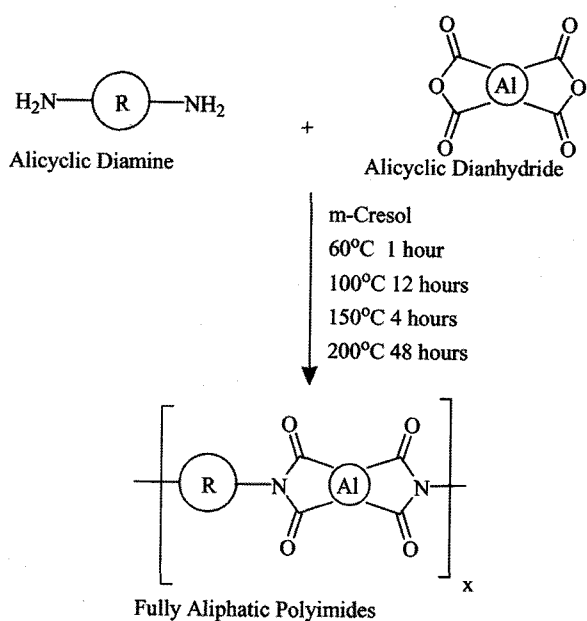


Figure 3. Monomers selected for the synthesis of APIs.^{58,59,66-72}



Scheme I. Scheme of synthesis of fully APIs.

Synthesis of Fully Aliphatic Polyimides

Polyimide synthesis can be carried out in two ways. First is the commonly used two step synthesis where the dianhydride and diamine are reacted in room temperature to give poly(amic acid) (PAA) and then the thermal imidization at elevated temperatures to convert the PAA formed to PI. But generally, the reaction of anhydrides with highly basic diamines, such as aliphatic and alicyclic diamines, provides amic acids, and then free amines form carboxylic acid salts with carboxyl group of amic acids due to their high basicity.⁹⁰ In the polymerization, salt formation prevents the attainment of high molecular weight PAA. In fact, the polymerization, which was carried out in polar aprotic solvents, such as *N*-methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylacetamide (DMAc), provided the low-molecular-weight PAAs whose inherent viscosities were 0.07-0.08 dL g⁻¹.

One Step Synthesis. Recently, it was found that the soluble PIs with large molecular weight can be produced in a single step.^{91,92} A one-pot PI synthesis without isolation of PAA at high reaction temperature would be a useful method

for preparing high molecular - weight APIs, because the amines used for the salt formation can be generated during the formation of imide. The cyclodehydration into imide form is completed in the solution state, and a relatively mild reaction temperature is used, for instance, 160-200 °C, which might avoid several possible side reactions that might occur during the curing process in high-temperature solid phase.⁹³⁻⁹⁵ High temperature polymerization was carried out in an aprotic solvent, such as NMP or DMAc. The APIs with inherent viscosities of 0.07-0.08 dL g⁻¹ were obtained, however. One-step synthesis of PIs is successfully carried out in *m*-cresol. The synthesis method used for the preparation of fully APIs by Mathews *et al.* is given in Scheme I. A typical example of the polymer synthesis procedure is as follows. A solution of equimolar amount of diamine and dianhydride in *m*-cresol was heated in the following steps: 100 °C for 12 h, 150 °C for 4 h, and 200 °C for 48 h. The solution was then cooled to ambient temperature, diluted with *m*-cresol, and poured into methanol. The polymer was filtered off and dried *in vacuo* at 60 °C.

Film casting of the PIs formed can be done as follows. A 5-7 wt% solution of polymer in chloroform or DMF was prepared and filtered to remove the non-dissolved materials and dust particles and was poured into a Petri dish. The casting process took about 8 h at room temperature. The casting films were dried in an oven at 40 °C for 6 h without vacuum and for another 6 h with vacuum, and the resulting films samples were dried at 80 °C for 6 h and then at 100 °C for 10 h. To perform the dielectric constant and transparency measurements, the solutions of APIs after dissolving in CHCl₃ were spin-coated onto clean ITO glass and quartz plates, respectively, and then subjected to the heating cycle described above. To improve the film forming efficiency while spin coating pretreatments can be done to the ITO and Quartz plates. The quartz plates were cleaned with diluted water and then with hot piranha solution (7:3 M ratio of conc. H₂SO₄ and 30% H₂O₂) and the ITO plates were washed using a detergent bath in an ultrasonicator for at least 30 min, and then thoroughly rinsed with distilled water, dried, and stored in a nitrogen filled glove box. Before coating the PI solution onto ITO, the coated sides of the electrode were subjected to plasma and immediately spin coated with the polymer.⁷¹

Synthesis of Wholly Alicyclic Polyimides by Silylation Method. Watanabe *et al.*^{66,68} and Oishi *et al.*^{72,96} reports the synthesis of fully APIs by silylation method. In the former study diamines, 5-amino-1,3,3-tri methylamine and 2,5 (2,6)-bis (aminomethyl) bicycle-[2.2.1] heptane, were selected and silylated with trimethyl silylchloride in presence of triethylamine in toluene to get *N*-silylated alicyclic diamines. The polyaddition of *N*-silylated diamines to tetra carboxylic dianhydride produced poly(amic acid silyl ester)s (PASE)s having high molecular weights without formation of any salts during polymerization. In spite of the advantages of the

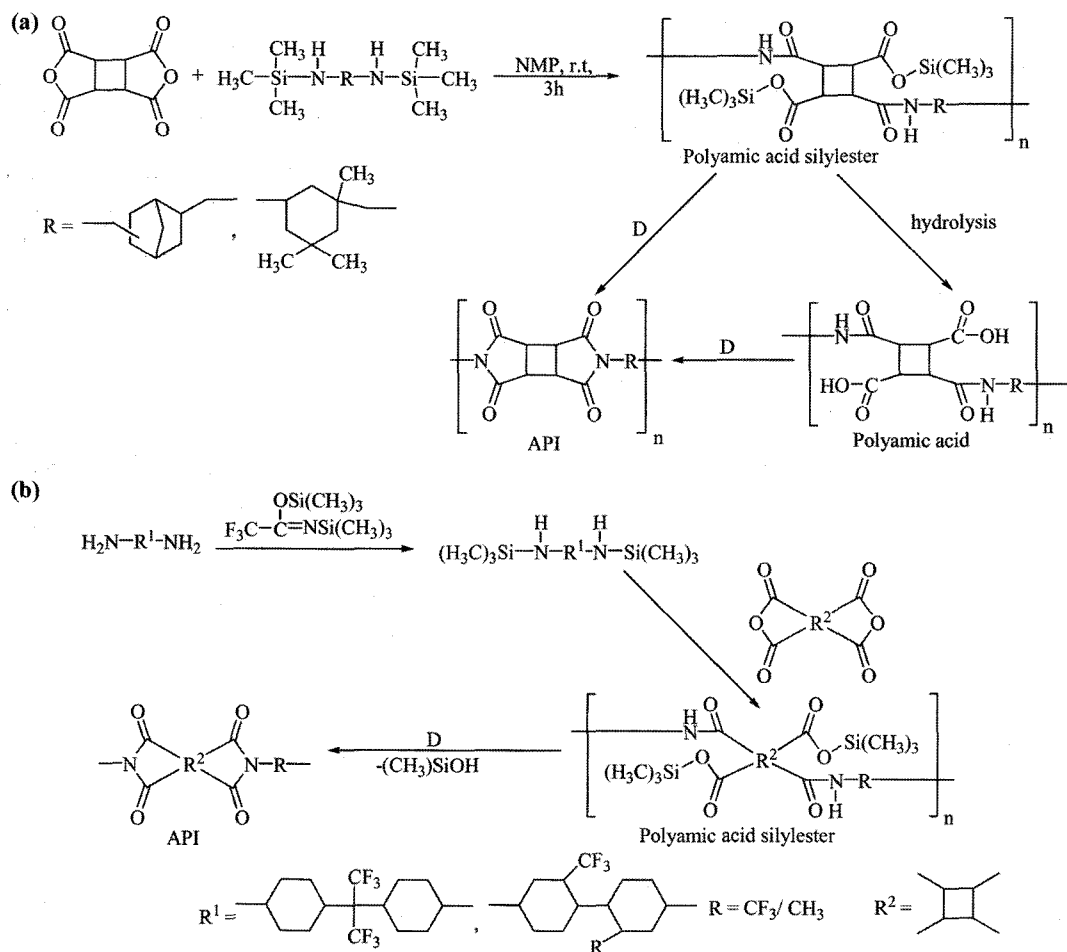
silylation method, the main drawback of the use of *N*-silylated alicyclic diamine as API-forming monomer is a relatively complicated handling because of their tendency to be hydrolyzed. This demerit is solved in the latter work where the synthesis of wholly alicyclic PIs is done through *in situ* silylation method by the use of amide type silylation agent. The reaction procedure is demonstrated in Scheme II.

The silylation method employs two steps. The ring opening polyaddition of the *N*-silylated alicyclic diamines to alicyclic dianhydrides, producing PASE, which in turn undergo subsequent thermal imidization to form APIs. The first step of polymerization proceeded smoothly in homogeneous solutions without any salt formation, giving the clear and viscous PASE solutions. The inherent viscosity of the PASE ranged between 0.3-0.74 dL/g indicating enough molecular weights to form cast films. Thus formed PASE was subjected to thermal imidization by heating at 200 °C for 1 h, 250 °C for 1 h and 300 °C for 1 h to be converted to wholly alicyclic PI films by the elimination of trimethyl silanol.

Structural Confirmation of Fully Aliphatic Polyimides. Structural confirmation of a fully API can be done using FTIR and NMR spectroscopies and by elemental analysis. Figure 4 presents a representative FTIR spectrum of a fully API reported by Mathews *et al.* The characteristic peaks occurs at 1780 (C=O symmetric stretching), 1716 (C=O asymmetric stretching), 1375 (C-N-C stretching), 739 (imide ring deformation), 2800-2900 (aliphatic C-H stretching), 1465 (CH₂ bending), and 1450 and 1395 cm⁻¹ (CH₃ bending). The slight shifts of the absorption peaks from the usual wavenumber values can be attributed to the nonconjugation due to the absence of aromatic ring.

The major difference between the pure APIs and silicon containing fully aliphatic polyimidosiloxanes is the bands of Si domain stretching between 1000 and 1180 cm⁻¹ together with around 850 cm⁻¹ (Si-O-Si asymmetric stretching), around 1400 cm⁻¹ (Si-H₃), and at 787 cm⁻¹ (Si-C). The intensities of these bands gradually increases as the amount of APTMS residue increased in the PI backbone, while the intensity of the absorption bands corresponding to that of aliphatic moieties decreased.⁷¹

In addition, NMR spectra can be also utilized for the structural confirmation of synthesized fully APIs. The APIs shows all the characteristic peaks corresponding to the dianhydride and diamine residue which constitute its backbone. The copolyimides showed all the characteristic peaks of the monomer residues which constitute its backbone. The C=O bonds of the imide ring plays an important role to distinguish the homo and copolyimides. The homo-polyimides gives single peak around 176 ppm in ¹³C NMR spectra, while in the case of copolyimides those C=O peak splits due to the difference in the carbon attached to the two sides of the imide group. The NMR integration method can be also utilized to determine the exact ratio of the monomer residues in the PI backbones. Mathews *et al.* synthesized vary-



Scheme II. Synthesis of wholly alicyclic polyimides from (a) *N*-silylated alicyclic diamines and (b) *in situ* *N*-silylated fluorinated alicyclic diamines.^{66,68,72,96}

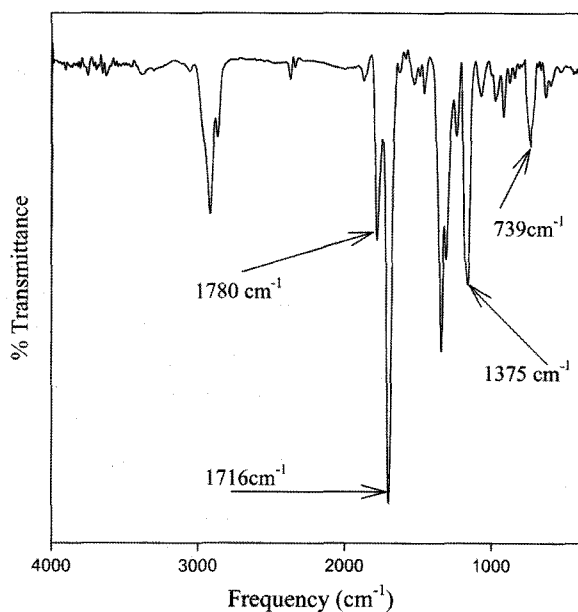


Figure 4. IR spectrum of a representative fully API.

ing compositions of fully aliphatic polyimidosiloxanes using the diamines **10**, **11**, **12** or **13** with **17** given in Figure 3 and the stoichiometry of the reactants was controlled by ^1H NMR by comparing a specific proton signal for monomer residues. For **10**, the peak at 1.6 ppm, **11** that at 1.06 ppm, **12** the proton at 1.32 ppm, and for **13** the peak at 1.4 ppm were chosen as the standards for comparison with the siloxane peak at 0.41 ppm to give relative composition of **17** and alicyclic units. The varying composition of the backbone was thus clarified by the ^1H NMR integration method.

Fully aliphatic polyimidosiloxanes (APISiOs) are also characterized using ^{29}Si -MAS NMR spectra as presented on Figure 5. The ^{29}Si -MAS NMR spectroscopy showed the signals of the internal silicon atoms of the polymer backbone around +7.6 ppm corresponding to $\text{Si}(\text{CH}_3)_2\text{-O-Si}(\text{CH}_3)_2$. The signal located around +7.6 ppm is attributed to the silicon atom close to the methylene group.⁹⁷ The ^{29}Si -MAS NMR spectrum of homo-polyimides with only dianhydride and siloxane residues exhibits a narrow single peak at +7.6 ppm. The narrow peak results from a single ordered

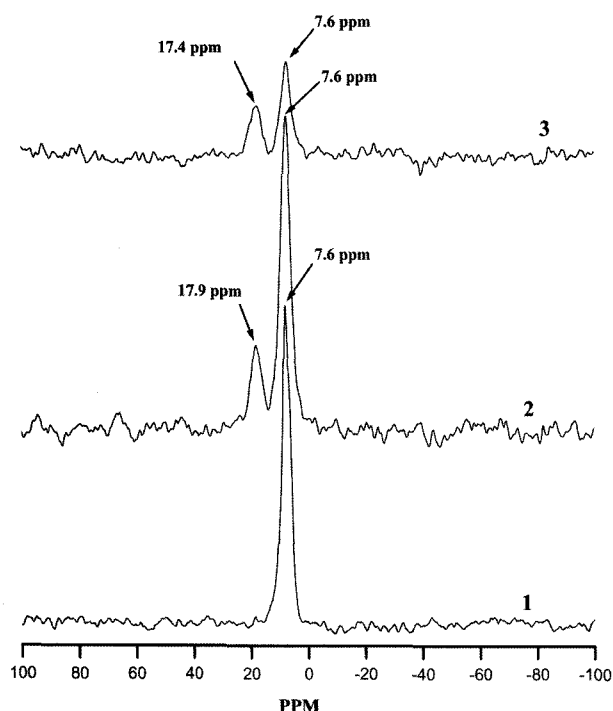


Figure 5. ^{29}Si -MAS NMR spectra of fully aliphatic polyimido-siloxanes synthesized in literature.⁷¹

environment around Si. The spectrum of copolymers exhibits two broad peaks around +17.5 and +7.6 ppm. Multiple peaks are the result of disordered atmosphere around Si atom.⁹⁸ The peak widths increase with increasing alicyclic diamine components, which suggests increasing disorder accompanying addition of cyclohexane or adamantane moieties. The peak near +17.5 ppm is due to the enhanced segmental motions.⁹⁹ This result indicates that the chain mobility of homo-polyimidosiloxanes is restricted and the incorporation of the alicyclic moieties enhances the mobility of the siloxane group of the polymer.

Properties of Fully Aliphatic Polyimides. The intrinsic viscosity measurements and the gel permeation chromatography (GPC) are used to confirm the formation of high molecular weight PIs. The intrinsic viscosities of fully APIs synthesized via one step synthesis ranged from 0.16–0.56 dL/g. For one step synthesis the polymer precipitation occurred when rigid diamines were used thus limiting the molecular weights of their corresponding homo-polyimides. The viscosity of the linear APIs increased upon incorporating adamantyl groups, presumably because of their bulkiness. In contrast, the viscosity of the alicyclic PIs decreased upon incorporation of bulky adamantane moieties, because they sterically hindered the polymerization reaction. According to GPC data, M_n and PDI of the PIs ranged from 2,400 to 45,200, and 1.1 to 2.4 respectively. Unfortunately the values of very rigid backbone API cannot be obtained because of their low solubilities. The lower M_w/M_n values

comparative to those of conventional PIs may be due to the somewhat low reactivity of monomers containing the rigid and bulky groups.¹⁰⁰ The PASEs which are the intermediate for the synthesis of fully APIs via silylation method gives intrinsic viscosities between 0.51 to 0.99 dL/g. The chromatogram indicated that the M_n and M_w values were in the range of 29,000 and 64,000 respectively, with respect to polystyrene standards and the ratio M_w/M_n was found around 2.2.

The good solubility of fully APIs is their first advantage over aromatic ones. The homopolyimides obtained from rigid monomers were soluble only in *m*-cresol and sulfuric acid because of the rigidity of their backbones. Copolymerization of both rigid and flexible diamines produced APIs that had improved solubility relative to those of the corresponding single diamine PIs. Enhanced solubility in PIs is generally governed by the presence of flexible backbones, bulky non-coplanar groups, and kink linkages; all of these factors reduce the degree of polymer chain interaction and their rigidity.¹⁰¹ In this case, the improved solubility of the copolyimides clearly arose from the presence of a flexible aliphatic backbone together with the bulky adamantyl moieties, which create steric hindrance and curtail both inter-chain interactions and chain packing. For fluorine containing APIs the homopolyimides were not soluble in any organic solvents but the copolyimides were found to be slightly soluble in *N,N'*-dimethylacetamide (DMAc), NMP and 1,3-dimethyl-2-imidazolidone (DMI). As a result of incorporation of siloxane groups to the solubility of the PIs were found to increase till certain ratio after that the solubility decreased because of the increased interactions.

Wide-angle X-ray diffraction (WAXD) measurements are used to evaluate the crystallinity and correlate with solubility of fully APIs. Figure 6 displays representative WAXD results. All of the APIs exhibited peaks in the region $2\theta < 20^\circ$, which indicates that they possess crystalline structures as well as intermolecular regularity. The linear aliphatic diamine-based APIs presented patterns in the region $2\theta < 20^\circ$ that are different from those of the alicyclic APIs. The broad peak centered at $2\theta = 16.02^\circ$ (d-spacing = 5.5 Å) shifted to a lower position and split into several smaller peaks when changed the diamine from 1 to 2. In addition, the peak intensity increased as the chain length of the PI backbone increased; this finding suggests a high degree of internal order. Alicyclic APIs exhibited a peak at $2\theta = 16.54^\circ$, which corresponds to a d-spacing of 5.3 Å. Incorporation of adamantyl moieties into the alicyclic and APIs resulted in a lowering of the peak intensity and broadening of the peaks at $2\theta < 20^\circ$. The decreased scattering intensity suggests a disruption of the internal order; the broadening of the peaks arises from the lattice strain¹⁰² that result from the presence of the bulky and rigid pendent adamantane groups. The broad peak is due to the diffraction of a poor intermolecular packing combined with amorphous halo.¹⁰³ A lower

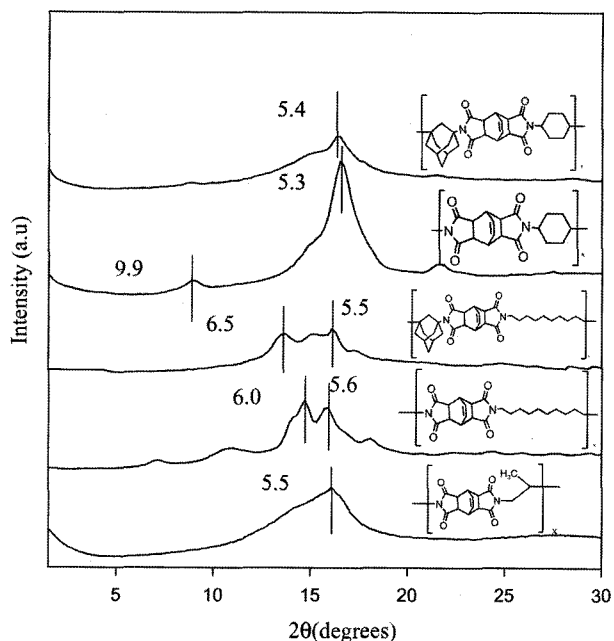


Figure 6. X-ray diffractograms of APIs. The structures of the polymers are presented above the corresponding curves.⁷⁰

crystallinity is for the copolyimides containing 1,3-diaminoadamantane with respect to the alkyl chain length as a result of and 3,3'-diamino-1,10-diadamantane residues, presumably because of the low degree of dipolar interchain interactions between the bulky moieties; this result is consistent with their higher solubility.

As the siloxane unit was incorporated the peaks at $2\theta < 20^\circ$ disappeared and the amorphous halo was evident at $9^\circ < 2\theta < 40^\circ$. The intermolecular distance which was estimated from the maxima of the broad peak at $9^\circ < 2\theta < 20^\circ$ increased slightly and while the peaks broadened as a result of lattice strain as the amount of siloxane group was raised. But as the amount of Si units increased slight sharpening of the amorphous halo and appearance of peak at 5.2° (d-spacing 16.4 Å) was observed, pointing the regain of ordered internal arrangement in APISiO chains. For APISiOs with adamantane units only a broad amorphous halo over the range $10\text{--}20^\circ$ (2θ) was seen, indicative of the existence of a very poorly developed crystal structure. Homo-polyimidosiloxanes containing siloxane diamine residue only showed 7 distinct diffraction peaks at $2\theta = 7.8, 11.7, 14.52, 16.65, 18.61,$ and 27° corresponding to d-spacing of 11.3, 7.5, 6.07, 5.3, 4.8, and 3.3 Å respectively. The splitting of the broad peak at $2\theta < 20^\circ$ points high intermolecular regularity and chain packing arising from the highly flexible nature of the siloxane containing diamine group.

Low dielectric constant is the second advantage of fully APIs over aromatic PIs. One method to determine the dielectric constant is from capacitance, using the formula $K = Cd/A\epsilon_0$, where C is the observed capacitance, d the film thick-

ness, A the area, and ϵ_0 the free permittivity. The homopolyimides derived from aliphatic linear diamines had comparatively high ϵ (2.92-2.56) values because of their higher degree of close chain packing; the values decreased proportionally with respect to the alkyl chain length as a result of diminution in the degrees of chain packing and interchain interactions. Inefficient chain packing, which induces free volume, is the reason for the lower values of ϵ for the alicyclic PIs. Among the constitutional ortho and para isomers of diamino cyclohexane (monomers **5** and **6**), the API derived from the ortho isomer possessed the lower value of ϵ , possibly because of its higher free volume. The dielectric constants decreased further for the APIs based on **10** and **11**; of these systems, the presence of the methyl-substituted bis-cyclohexane moiety led to a much lower value of ϵ as a result of its greater free volume. The copolyimides containing adamantyl moieties possessed the lowest values of ϵ (2.8-2.4) which can be attributed to the presence of the highly rigid and bulky alicyclic moieties, which sterically hinder the packing and enlarge the free volume in the PIs. Unexpectedly, the values of ϵ of the APIs containing biadamantyl groups were higher than those of the APIs containing adamantyl groups, regardless of the increased dilution of the polar imide groups that is caused by the more-bulky biadamantyl moieties. This finding is explained on the basis of the linear structures of the biadamantane-containing APIs relative to those of the non-coplanar adamantane-containing APIs; i.e., the former species have smaller molar volumes. In general, an increased free volume correlates with a decreased dielectric constant for these APIs, except for the rigid adamantane-based homopolyimides.

Another method of determination of dielectric constant is from refractive index (n). An average refractive index is calculated using the equation, $n_{AV} = (2n_{TE} + n_{TM})/3$, where n_{TE} and n_{TM} are the in-plane and the out-of-plane refractive indices respectively. Birefringency (Δn), which is related to the degree of orientation or the refraction units, given as the difference between n_{TE} and n_{TM} , provides additional information regarding the orientation effect of PIs. A dielectric constant (ϵ) of material at optical frequencies can be estimated from the refractive index n according to Maxwell's equation, $\epsilon = n^2$. The ϵ around 1 MHz has been evaluated as $\epsilon = 1.10 n_{AV}^2$, including an additional contribution of approximately 10% from the infrared absorption.^{104,105} The decreasing aromatic character of PIs decreases the refractive index and birefringency there by decreasing the dielectric constant. For the effective comparison of the dielectric constants and refractive indices and birefringency of fully aliphatic, semi-aromatic and fully aromatic PIs we have tabulated the results found in literature 58 and 68 in Table I.

The negligibly small birefringency of semi- and non-aromatic PIs implies that the polymer chains are randomly oriented in the film due to a weak polymer-polymer interaction. The average refractive indices (n_{AV}) of the PIs prepared via

the silylation method were determined between 1.5173-1.4977. The n_{AV} of 1.5173 and 1.4977 can be translated into dielectric constants of 2.53 and 2.47, respectively. These values are slightly lower than the optically estimated ϵ of an alicyclic PI (2.55)¹⁰⁷ and a fluorinated semiaromatic PI (2.6)¹⁰⁶ and significantly lower than that of a semiaromatic PI (2.83).¹⁰⁷ In addition, the in-plane/out-of-plane birefringences (Δn) of the PIs were estimated as 0.0004-0.0000.

This negligibly small birefringence implies that these polymers have low polarizability anisotropy and the polymer chains are randomly oriented in the film. The absence of birefringence was also reported for an alicyclic PI.¹⁰⁷ The fluorinated PIs synthesized by Oishi *et al.* displays Δn , n_{AV} , and ϵ in the range 0.0016-0.0128, 1.471-1.478, and 2.38-2.40 respectively. The influence of Si content as well as that of adamantane units upon ϵ of APISiOs is demonstrated in

Table I. Optical Properties of Polyimide Films

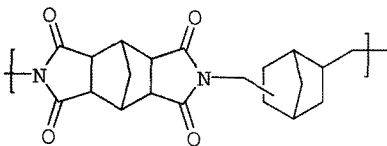
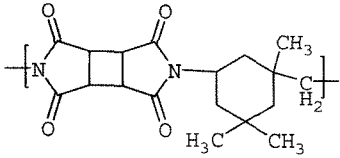
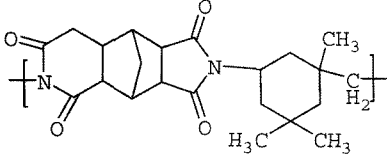
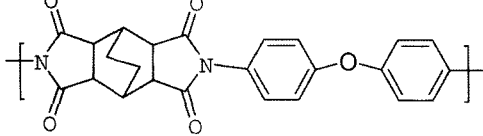
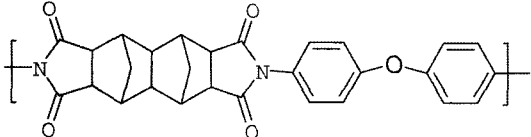
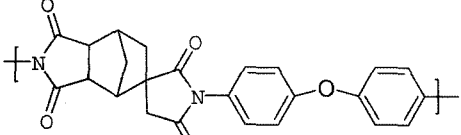
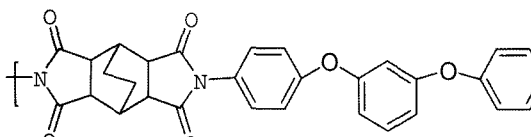
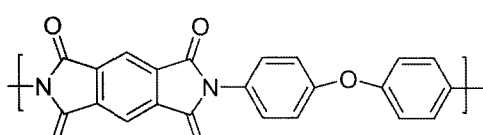
Polyimide	Category	n_{AV}	Δn	ϵ	Ref
	Fully aliphatic	1.52	0.000	2.55	58
	Fully aliphatic	1.49	0.000	2.47	68
	Fully aliphatic	1.51	0.004	2.53	68
	Semi-aromatic	1.61	0.000	2.87	58
	Semi-aromatic	1.60	0.013	2.83	58
	Semi-aromatic	1.61	0.015	2.85	58
	Semi-aromatic	1.59	0.017	2.81	58
	Fully aromatic	1.68	0.079	3.13	58

Figure 7. Such low dielectric constants are due to the fact that those polymers are fully aliphatic, subsequently having low hydrophobicity and polarity. As the amount of siloxane group increased in polymer chain the dielectric constant decreased first. This can be explained in terms of an overall enhancement of small scale molecular mobility by the incorporation of silica domains in the polyimidosiloxanes backbone, arising from loosened molecular packing of API-

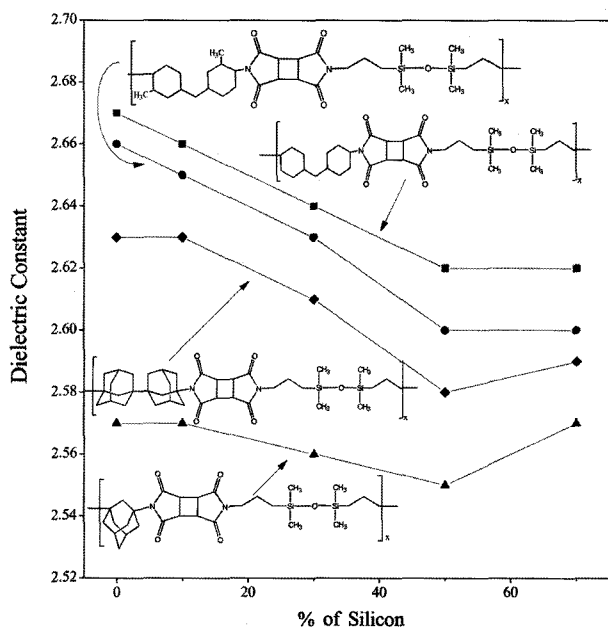


Figure 7. Trends in dielectric constants of APISiOs.⁷¹

SiO chains as compared to API chains.¹⁰⁸ But as the amount of siloxane units increased no further decrease in ϵ value was seen owing to the improved degree of close chain packing.

Fully APIs in doubtfully owe high transparency due to low molecular density, polarity and rare probability of inter and intra molecular charge transfers. These factors should have contributed to make transparency of all the synthesized APIs above 80%. Further enhancement in transparency around 95% as a result of the incorporation of adamantyl or fluorinated groups can be attributed to loosening of intermolecular packing due to the low polarizable and bulky pendent groups. But Si content adversely affected the transparency of the polymers due to the interchain cross-linking nature of siloxane in the APISiO backbones. Figure 8 is the UV-Visible spectra given in literature⁵⁸ which pictures the difference between the transparencies of aromatic, semi-aromatic and aliphatic PIs.

The thermal behavior of the PIs was evaluated by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA). Aliphatic polymers generally show low thermal stability than aromatic polymers. However it was reported that alicyclic polymers containing a polycyclic structure showed similar thermal stability to aromatic polymers.¹⁰⁹ The APIs containing linear aliphatic chains on their backbones were found to be the least stringent to temperature and their stability decreased as thermally fragile alkyl chain length increased. The polymers showed 5% weight loss ranging from 242-270 °C. The temperatures for 10% gravimetric loss (T_{10}) that are important criterion for evalua-

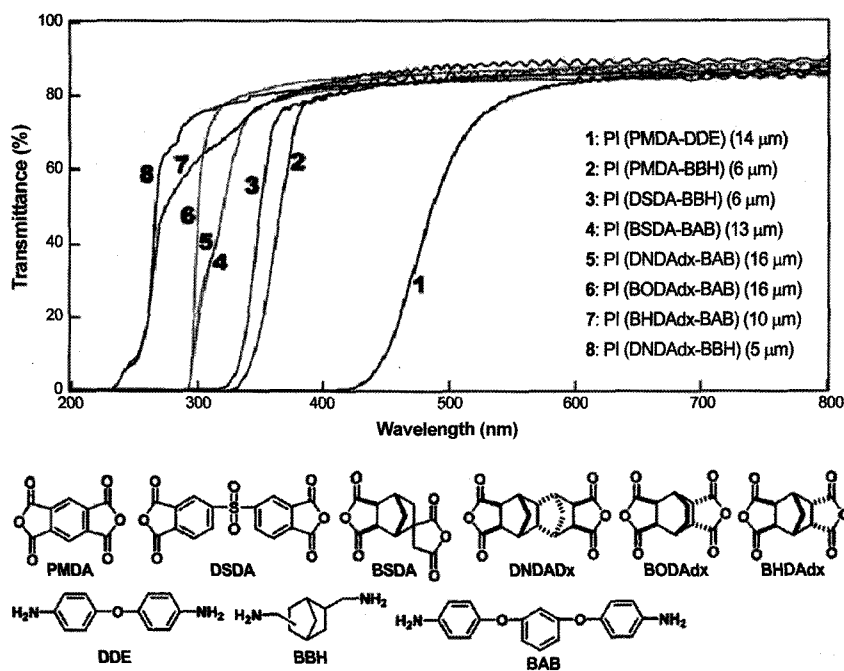


Figure 8. The transmission UV-Vis spectra of the free standing polyimide films. The film thicknesses are given in parentheses.⁵⁸

tion of thermal stability were in the range of 304-320°C. APIs containing **1** residue showed low thermal potency than those containing **2** backbones due to high imide chain separation arising from the methyl side chain of **1**. The copolymerization of aliphatic chain and rigid adamantyl groups results in polymers with higher thermal stability. Taking the rigidity factor into account it was assumed that the APIs based on adamantyl units will show the highest thermal stability. Despite the rigid backbones, the thermal stability of homo-polyimides derived from the diamines **12** and **13** were lower than that with other alicyclic diamines. This unexpected behavior may be due to the low degree of intermolecular interactions because of the steric hindrance provided by the bulky adamantyl groups. The PIs derived from alicyclic monomers showed appreciable thermal stability. The polymers showed 5% weight loss ranging above 400°C in nitrogen and above 350°C in air. The temperatures for 10% gravimetric loss (T_{10}) were above 450°C in nitrogen and above 400 in air. Fluorine containing wholly alicyclic PIs derived from monomers **14**, **15**, and **16** exhibited thermal decomposition temperatures (T_{10}) in the range of 395-400 in air and 430 to 440°C in nitrogen. The polymers containing siloxane groups underwent their 5% weight losses within the temperature range from 325 to 455°C. The temperatures for 10% gravimetric loss (T_{10} , were in the range 353-476°C. Thermal stability was further improved when silica was introduced. The APISiO containing 50% silica had the maximum T_d in the range 460-470°C. The increase in the thermal stability may be resulted from high thermal stability of silica and the pseudo-crosslinking nature of silicon particles.¹¹⁰ On the other hand too much amount of **17** affected contrarily since it increases the amount of thermally fragile aliphatic chains. Adamantane based polyimidosiloxanes showed enhanced thermal stability which can be attributed to the precise balance of rigidity and interchain interactions. Among them the biadamantyl based APISiOs have higher thermal resistance than those with mono adamantane units mainly because of the dilution effect of aliphatic imide moieties. In addition, APISiOs containing consecutive adamantyl units have linear structure compared with those containing an adamantyl unit. These results suggest that the synthesized fully APISiOs have such high thermal stability, though not as high as those derived from aromatic monomers, as being suitable for electronic materials.

The thermogravimetric curves were also used for estimating the proportion of siloxane units in the polymer chain by Mathews *et al.* The char yield at 600°C was estimated from the curves. The increase in final weight residue suggests the successful incorporation of higher amount of silica into polymer backbone. The varying ratios of APTMS and alicyclic diamine residues in the synthesized APISiOs were confirmed by comparing the experimental and theoretical char yield. Theoretical values are calculated on the assumption

that every Si atom can be converted into silicon oxide. These results indicate that though the thermal stability is less than aromatic PIs, they have still high stability suitable for electronic applications.

The glass transition temperatures was recorded according to the DSC thermograms of the second heating since the influence of residual water or solvent and the history of thermal annealing were occasionally observed in the initial DSC heating run. T_g s of the PIs were in the range 110-250°C although no T_g was detected for the most rigid homo APIs derived from **5**, **6**, and **12**. PIs containing linear aliphatic residues of **1**, **2**, **3**, and **4** showed a melting temperature around 320-380°C and T_g in the range 110-190°C, which reappeared with repeated scans. This means that these PIs have a semicrystalline nature. For all the other APIs, no melting transitions was observed in the 70-400°C range, presumably because they have T_m s above 400°C or decomposed before T_m . T_g s of copolyimides shifted to higher temperatures due to bulky adamantane groups inhibiting chain mobility together with the generation of free volume. The glass transition temperature of copolyimides containing highly rigid alicyclic and adamantyl moieties was not observed by DSC proving them to be largely or totally amorphous in nature. The fluorinated APIs showed higher T_g s in the range 306-335°C. In general, the increased chain rigidity due to the pendent cardo groups restricted the free rotation about the polymer backbone to yield polyimidosiloxanes with high glass transition temperatures. As the amount of silicon increased in the PI backbone, glass transition temperature showed an increasing trend followed by a decrement when the APTMS amount further increased. According to the previous report,¹¹¹ even when a small amount of silicon is introduced into PI matrix scales down the T_g notably due to the plasticizing effect of low molecular weight silica. The incorporation of **17** should have limited the chain motion leading to the enhancement of T_g . But as the amount of siloxane rose again, the plasticizing effect should have imparted better influence as evidenced by the decrease of T_g .

The mechanical properties of the fully APIs can be investigated using the stress-strain curves obtained from universal testing machine (UTM) or thermo-mechanical analysis (TMA). The API films possess a tensile modulus of 1.3-3 GPa, tensile strength in the range of 78.7-145 MPa and elongation at break around 3.4-30%. Most of the PIs showed exhibited appreciable tensile strength, indicating they are mechanically stringent. The UTM traces for highly rigid APIs were not measured because the films were too brittle. The flexible films obtained showed strong and tough nature. Tensile strength of the flexible APIs was enhanced as a result of the incorporation of adamantane moieties which improve the rigidity of the polymer chain. A special trend was not noted on tensile strength on increasing the amount of Si for API-SiOs, except that the tensile strength shows a maximum for

the 1:1 ratio of APTMS and alicyclic diamines. For PI/silica hybrid networks, the strength and toughness of the hybrid is dependent on the density of the physical crosslinking between PI molecules and silica networks. In an appropriate range of the crosslink density, the crosslinks could exhibit the strengthening and toughening effects.²¹ Unlike hybrids, when siloxane groups are directly bonded to the PI backbone chemically the balance of chain rigidity, flexibility, and interchain interactions plays important roles effectively to maximize the tensile strength. As the amount of siloxane units increased, the tensile strength was decreased maybe due to the less tough linear aliphatic unit enhancement in the chain. On the other hand, the elongation at break went on increasing as the number of the flexible units increased.

Concluding Remarks

This study on fully APIs reveals a number of interesting facts. PI investigations have mainly concentrated on wholly or partially aromatic PIs. Though aromatic PIs show excellent thermal stability, chemical resistance, and mechanical properties, their insolubility in common solvents in the fully imidized forms, light or dark yellow color of films due to intra- and inter-molecular charge transfer (CT) interactions and high dielectric constants are the main obstacles that hinders their extended application in optoelectric materials and high speed multilayer printed wiring boards. These demerits of aromatic PIs have given rise to the incorporation of aliphatic moieties to aromatic backbones and the synthesis of fully APIs. The partially APIs have properties in between those of aromatic and aliphatic ones. The film formation ability of partially APIs is better than that of fully aliphatic once because the films formed by APIs are sometimes too brittle. In comparison with commercially available PIs (Ultem® 1000; $T_g = 215^\circ\text{C}$, tensile strength = 105 MPa), the APIs were found to have high T_g up to 350°C . The highest values of glass transition temperature and tensile strength was found for copolyimides presumably because of a balance between stiffness, polarity, and free volume of their backbone units. The copolyimides of alicyclic and adamantyl diamines or fluorinated or siloxane containing diamines exhibited dielectric constants as low as 2.34-2.56, while possessing enhanced solubilities and transparencies. Even the commercialized PI, Kapton® has ϵ value around 3, together with the demerits that they are insolubility in organic solvents and are highly colored. APIs shows superior properties like low dielectric constant (2.44-2.5) together with excellent solubility in common organic solvents and high transparency c.a. 90%. Transparent PI films have appreciable thermal stability and seem suited for application to the construction of optical devices, rather than using aromatic PIs possessing aliphatic, alicyclic or alkynyl side chains. Because of the low hydrophobicity and polarity of the rigid and bulky adamantane units, together with the flex-

ibility of the alicyclic chains, the copolyimides are quite soluble in common organic solvents and, therefore, they can be processed directly. The adamantane-based APIs rank superior to the bisadamantane-based PIs because of their higher solubilities, values of T_g , and transparencies and their lower dielectric constants, but their thermal and mechanical stabilities were lower because of weak interchain interactions. Among the wide studies on PI/silica hybrid materials a different method of chemically implanting siloxanes into PI backbones can be considered. Unlike the widely used sol-gel process of physically interlocking PI and siloxanes with the chances of preferential hydrolysis, microheterogeneity, cracking, and delamination¹¹² one step poly(condensation/addition) reaction for synthesizing fully API-siloxanes. World-wide research is progressing for a practically applicable PI candidate devoid of demerits; despite the bewildering number of candidate materials under investigation, a clear winner has yet to emerge. The balance among stiffness, polarity, free volume, flexibility and silicon or fluorine content of their backbone units enables APIs to find immense range of applications in flexible polymer light emitting diode substrates, soft-printed circuit boards, interlevel dielectric insulators, high-speed passivation or dielectric films, and alignment films.

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