CHAPTER 1

INTRODUCTION

1.1 POLYIMIDES

Polyimides are a sophisticated family of materials, which cover an exhaustive range of high performance polymers. They find applications in highly technical end use fields from aerospace to microelectronics. Their diversity is such that it leads them into applications as fibres, films, moulding powders, coatings and composite prepregs where their major advantage, a high resistance to heat, places them in a niche other polymers cannot enter. Because of their performance and end uses, polyimides tend to be looked on as new to the polymer field, but they have been commercially available for over 25 years. Their strength and resistance to heat and chemicals are so great that these materials often replace glass and metals, such as steel, in many demanding industrial applications. They are even used in many day to day applications: they are used for the struts and chassis in some cars as well as some parts under-the-hood because they can withstand the intense heat and corrosive lubricants, fuels, and coolants cars require. They are also used in the construction of many appliances as well as microwave cookware and food packaging because of their thermal stability, resistance to oils, greases, and fats, and their transparency to microwave radiation.
1.1.1 Polyimide Properties

There was excitement when polyimides were introduced by DuPont in the 1960s. The structural composition of aromatic polyimides consists primarily of heterocyclic imide and aryl groups, which are linked sequentially by simple atoms or groups (Critchley et al 1983), as shown in Figure 1.1.

![Figure 1.1 Structural composition of aromatic polyimides](image)

The charge transfer works not only between adjacent units in the polymer chain, but also between chains as shown in Figure 1.2. The chains will stack together like strips of paper, with donors and acceptors paired up. This charge transfer holds the chains together very tightly, not allowing them to move around very much. When things can not move around on the molecular level, they can not move around in the whole material. This is why polyimides are so strong.
Figure 1.2 Charge transfer between polyimide chains

The structure within the polyimide which is responsible for the outstanding thermal and oxidative stability is the imide group. The combination of the imide structure with an aromatic structure gives the polymer a high glass transition temperatures ($T_g > 300^\circ C$), good oxidative stability, good mechanical strength and high modulus 2-4 GPa. The linearity and stiffness of the cyclic backbone allow for molecular ordering. This phenomenon results in lower coefficients of thermal expansion than those found for thermoplastic polymers having coiled, flexible chains (Numata et al 1985 and Hedrick et al 1997). Additionally, the morphology of long, linear ordered chains provides solvent resistance to the aromatic polyimides.

1.1.2 Types of Polyimides

Polyimides can be classified into three types and they are identified by synthesis methods.

- Condensation polymides – Non-melting and thermoplastic
- Addition polymides
- Hybrid polymides
1.1.2.1 Condensation polymides

Condensation polymers consist of two types, non-melting and thermoplastic systems.

**Non melting condensation** polyimides are based on pyromellitic dianhydride (PMDA) and aromatic amines, mainly oxydianiline (ODA). Du Pont have produced and marketed various polyimide forms based on the PMDA-ODA process. The Du Pont process yields a finely divided polyimide powder which can be formed under temperature and pressure into final shapes.

Other types of non-melting polyimides are produced from 3,3’,4,4’-benzophenone tetracarboxylic dianhydride (BTDA) and meta-phenylene diamine (MDA). This product is sold by Monsanto as SKYBOND and used as varnishes, coatings and prepregs for laminates.

Other BTDA based polyimides marketed are BTDA-MDA/DAP foam by Imitech, DuPont offer BTDA based coatings (PYRALIN). Other films are based on biphenyl tetracarboxylic dianhydride (BPDA) and aromatic diamines.

**Thermoplastic polyimides** are generally classified as thermoset resins, but by modification of the polymer chain, the thermoplastic characteristics for processability can be achieved.

General Electric introduced polyetherimide (Figure 1.3), ULTEM in 1982. This is an amorphous high performance engineering plastic which is melt processible. The imide units give good stiffness and heat resistance while the ether linkage provides the processing and melt characteristics allowing injection moulding, extrusion, thermoforming and blow moulding. The resin
is usually compounded with modifiers and reinforcements which alter the viscosity, aid moulding and provide extra stiffness, heat resistance and wear resistance.

![Figure 1.3 Polyetherimide](image)

Lenzing of Austria has marketed a polyimide based on BTDA-TDI/MDI, under the trade name P84. This product is sold by DuPont as finished parts for high temperature applications and composite tooling, under the tradename AVIMID N. It is also used as dielectric polymers under the PYRALIN tradename. AVIMID K is another composite material marketed by Du Pont for aircraft applications.

LaRC-TPI is produced by the reaction of 3,3′-diaminobenzophenone and BTDA in a suitable solvent at room temperature. This material is used as high temperature adhesive and as thermoplastic moulding compound.

### 1.1.2.2 Addition polyimides

Polyaminobismaleimides based on the N-substituted bismaleimides were synthesized by the reaction of bismaleimide monomer and diamine to give a linear chain extension using Michael addition reaction, and subsequently cross linked by a free radical catalyst and heat (Scheme 1.1).
Scheme 1.1 Reaction of bismaleimide with diamine

THERMID, produced by National Starch in America, is acetylene terminated polyimide used in coating, composite preps and inks, and is available as various types.

1.1.2.3 Hybrid polyimides

Hybrids contain other groups such as esters, amides, siloxane etc in their structure. The two main types are polyesterimides and polyamideimides. Polyesterimides are mainly used in magnet wire enamels, supplied by Schenectady under the name ISOMID.

In order to produce fusible polyimides Amoco introduced the amide moiety in the polyimide chain. This is a reaction between trimellitic anhydride and aromatic diamines. This results in a structure where the amide alternates with the imide link. The major use of these products is as coatings, or compounded with fillers and reinforcements as moulding compounds. Other
moieties can be incorporated and products containing siloxane (General Electrics SILTEM and Occidental’s OXYCHEM) are used for coating. Rohm and Haas have introduced imidized acrylics under the tradename of KAMAX.

1.1.3 Synthesis of Polyimides via Poly(amic acid)

Due to wide utility of polyimides in a number of applications, a broad range of synthetic routes have been developed. Polyimides are categorized as step-growth polymers, (Odian 1981, Cowie 1994, Ghosh and Mittal 1996 and Sperling 1992) which are formed from stoichiometric amounts of organic diamines and organic tetracarboxylic acids or derivatives thereof (Bower and Frost 1963 and Kreuz et al 1966) that can be either aromatic or aliphatic. Since the only requirement for polyimide synthesis is a diamine and tetracarboxylic acids or its derivatives, it can be quickly surmised that this creates a seemingly endless possibility for the creation of new polyimides. The reaction of diamine with tetracarboxylic acid or its derivative initially forms poly(amic acid) (PAA), which is then converted to polyimide. There are two stages in the synthesis of polyimide. The formation of PAA is carried out below 50°C in the presence of polar solvents. The low temperature prevents cyclization and maintains solubility.

The reaction mechanism forming PAA is shown in Scheme 1.2. Nucleophilic acyl substitution occurs at one of the carbonyl carbons of a phthalic anhydride. The attacking nucleophile consists of nitrogen from the aromatic diamine with its unshared pair of electrons. Bonding between the carbonyl carbon and the nitrogen results in formation of a cyclic intermediate, (1), with the pi electrons shifted onto the oxygen. This intermediate is short lived because the displaced electron pair shifts back to reform the carbonyl double bond, (2), and simultaneous bond-breaking occurs between the carbon and a “leaving group”. The bond that must break in this ejection step to give linear amide-acid is that which releases the central oxygen of the cyclic
intermediate (1), thereby giving a carboxylate leaving group. However, if
instead the bond breaks between the nitrogen and the developing \( \text{sp}^2 \) carbon,
the reaction is reversed to give the starting species - free amine and anhydride
groups. The rate of the forward reaction must be more rapid than the reverse
to achieve high molecular weight PAA. Since the carboxylate group is
chemically bonded, it cannot be systematically removed to drive equilibrium
in the forward direction. However, it can be “deactivated” through hydrogen
bonding with a basic solvent, such as N-methyl pyrrolidone (Pravednikov et

Scheme 1.2 Mechanism for formation of poly(amic acid)

Typical requirements for step-growth polycondensation reactions
must be met to obtain high molecular weight linear PAA (McGrath 1992)
viz.,

1. monomers must be highly pure (>99.9%)
2. one-to-one stoichiometry of monomers must be employed
3. monomers must be difunctional and reacting groups must be
   mutually accessible
4. length of reaction time must be sufficient for high conversion
(5) side reactions must be minimal or absent.

There are different methods of imidization of poly(amic acid). A brief account of each method is given below.

1.1.3.1 Bulk imidization or thermal imidization

This is the most neat and simplest method to imidize PAA. In a typical process PAA solution is cast over a substrate, often a glass plate, and thermally imidized by stage curing in a vacuum oven or in an inert atmosphere to obtain a polyimide film. The first pathway for cyclization of the amic acid moiety into imide involves gradual heating of poly(amic acid) up to 200-350°C. During this process, the solvent can be removed and water evolves as a by-product. Two possible mechanisms were proposed as shown in Scheme 1.3 (Harris 1990). This final annealing allows the chains enough freedom of motion to release nearly all the trapped water and solvent. The heating strategy used to convert the poly(amic acid) to the polyimide is significant for the following reasons. The trapped air and water evolved during the cyclodehydration reaction need time to diffuse out of the film. More importantly, the degree of imidization is extremely dependent on the mobility of the chains during this thermal treatment, which is dependent on (i) the concentration of residual solvent, (ii) the type of diamine and dianhydride moiety. The mobility of the chains is believed to be necessary for the nucleophilic substitution reaction between the amide nitrogen and carboxylic acid. Thermal imidization is widely used for preparing thin films, coatings, fibres, and powders since the solvent and by-product can be easily removed without generating voids and defects. Proper imidization procedure may eliminate cracks caused by shrinkage stress.
Chemical imidization is a method of choice, and accomplished using chemical agents as catalysts for ring closure at temperatures below that of thermal imidization, typically at room temperature (Vinogradova et al 1980, Endrey 1966 and Meyer et al 1996). The most commonly used dehydrating reagents are acid anhydrides, such as acetic, propionic, n-butyric, benzoic anhydrides, etc. in aprotic polar solvents or in the presence of tertiary amines. Commonly used amine catalysts include trialkylamines, pyridine, lutidine, and N-methylmorpholine. The reagent combination most widely used is an equimolar mixture of pyridine and acetic anhydride (Searl 1958, Roderick 1957 and Cotter et al 1961). The preferred product of the reaction, either a polyimide or polyisoimide, will be determined by the chemical reagent selection. Many factors, such as dehydrating agents, types of monomers, reaction temperatures, may affect the molecular weight of the
final polymer. Kinetic study of chemical imidization process led to a proposed mechanism (Scheme 1.4).

**Scheme 1.4  Mechanism of chemical dehydration of poly(amic acid)**

1.1.3.3  **Solution imidization**

This process is carried out in a high boiling point solvent between 160 and 200°C in the presence of an azeotropic solvent (McGrath et al 1991). Azeotropic solvents are typically used to remove water formed during the reaction and drive the reaction to completion. The solvent of choice needs to be capable of transporting water from the reaction. Typical azeotropic solvents are toluene, xylene and cyclohexylpyrrolidone. As the reaction proceeds, the end groups recombine and intrinsic viscosity increases to form high molecular weight polyimides.

1.1.3.4  **Ester-acid route**

In an effort to alleviate dianhydride water sensitivity and subsequent hydrolysis, ester-acids were employed instead of dianhydrides to synthesize polyimides. The diester diacid dianhydride derivatives can be synthesized from dianhydrides in alcohol in the presence of a tertiary amine
catalyst. Additionally, the diester-diacid is generally more soluble than the parent dianhydride (Serafini et al 1972, Moy et al 1993 and Tan et al 1997).

1.1.4 Polyimide Applications

Proper design of polyimides has led to their use in aerospace, microelectronics, automotive transportation vehicles and packaging industries. They are used as adhesives (Lindeberg and Hjort 2003 and Saeed and Zhan 2007), composite matrices (Thompson et al 2002), fibres (Sukhanova et al 1999), foams (Williams et al 2005), membranes and films (Brian et al 2005, Compton et al 2006 and Dasgupta et al 2010).

Polyimides have found great utility in wafer fabrication as photoresists and dielectrics, due to their excellent elevated temperature performance, corrosion resistance, and their ability to be spin coated onto substrates. They also serve as insulators, which prevent “cross-talk” between conducting vias, and as adhesives between polymer-polymer and polymer-metal interfaces. They may also be designed to nearly match the coefficient of thermal expansion of the supporting substrate, which is generally a metal or ceramic (Sillion and Verdet 1991). Photosensitive polyimides are used in electrical devices where a submicron pattern is needed to route electric current. They also greatly simplify the complex, multistep processing used in the high-resolution photolithography process needed for non-photosensitive materials.

Optical wave-guides are reflective channels, which allow information in the form of light to be transported through a medium by internal reflection. Optical wave-guides have the advantage of being able to transport multiple signals simultaneously without affecting each other and show immunity to electromagnetic interference and experience noninteraction when signals cross. Both free standing and embedded waveguides are well
known (Feger and Franke 1992). The process requirements for waveguide materials exceed those found in many thermoplastics. Polyimides, which are well known for their excellent thermal stability, good dimensional stability, and high decomposition temperatures, can satisfy these material requirements (Feger and Franke 1992). Polyimides that are thermally imidized from the poly(amic) acid were found to show a large optical loss, which is not suitable for the waveguide application. Upon poly(amic) acid cyclization to the polyimide and solvent removal, it was found microvoids formed causing density fluctuations and light scattering leading to an optical loss in the material. On the other hand, fully imidized polyimides show a significant reduction in optical loss. By introducing bulky side groups with fluorine substituents, the polyimide can be generated in the fully cyclized form. They also promote solubility, and hinder chain ordering and charge transfer, all of which are favorable for this application (Feger and Franke 1992).

Polyimide composites surpass mechanically fastened assemblies in terms of fatigue and corrosion resistance, aerodynamic properties, manufacturing costs, and repairs. Due to these outstanding properties and economical advantages, polyimides are used in the aerospace industry as struts, brackets, composites, and structural adhesives.

Polyimide adhesives fall into one of three classes based on their adhesion characteristics (Feger and Franke 1996). The first class is amorphous polyimides, which self-adhere and bond well with metals such as copper, chromium and aluminium. Semicrystalline polyimides form the second class of polyimide adhesives. This class adheres well to reactive metals such as aluminium and chromium, but not to unreactive metals such as copper. Some semicrystalline polyimides also exhibit marginal self-adhesion. Thermosetting resins represent a third class of polyimide adhesives. Low molecular weight polyimides with curable endgroups allow for good wetting
and adhere well to metals, ceramics and to themselves, if one of the layers remains uncured prior to adhesive bond formation (Feger and Franke 1996).

The outstanding thermal and chemical resistance of polyimides has promoted their use as spin-on dielectric films for isolating metal lines in multilevel electronics packaging. One important function of the dielectric film is to block electromagnetic interaction between parallel metal conducting lines that are operating independently (called “cross talk” noise) (Feger and Franke 1996). For effective blocking, the film must have low electrical conductivity/permittivity. Materials having dielectric constants of less than 4.0, the value of the standard silicon dioxide insulator, have been recognized by the electronics industry as being superior in electrical performance to ceramic materials. The dielectric constants of aromatic polyimides, such as Kapton-H, approach 3.0 (when dry), which has led to widespread use of these materials as thin film insulators.

Polymides for microelectronic applications have attracted a great deal of concern in the past few years because they can be applied to the manufacturing of various flexible and low-cost electronic and display devices. They have excellent thermal and chemical stability, good mechanical strength, good dimensional stability, low dielectric constant, and large flexibility (Ho et al 1982, Chao et al 1989, Tummala and Rymaszewski 1989, Ramos 2002 and Kim and Lee 2006). As a result of these properties, they have been utilized in metallic conductor substrates, tape automated bonding and flexible printed circuits. A printed circuit board (PCB) is a micro-thin conducting circuit of either the rigid or flexible type, which is fabricated on a dielectric board for locating electronic devices. A flexible PCB (FPCB) has many advantages compared to a rigid board. The flexible printed circuit board is light, soft, thin, small, ductile and flexible, and possesses high wiring density. The flexible printed circuit board can be three-dimensionally wired
and the shape of the flexible printed circuit board can be changed according to space limitations. Hence it is typically useful for electronic packages where flexibility, weight control and the like are important. In many high volume situations, flexible circuits also provide cost advantages associated with efficiency of the manufacturing process employed. Flexible circuits are most commonly used in board-to-board, board-to-chip, and chip-to-chip connections in packages having limited space and stacked rigid boards, thus requiring three-dimensional connections. Flexible circuits are largely used in portable electronic products, such as notebook, mobile phone, personal digital assistant and information appliance. For example, the flexible printed circuit board can be used as a connection between a liquid crystal display, a floppy disk driver, a hard disk driver or a compact disc read only memory driver to a motherboard. Flexible copper clad laminate (FCCL) is generally employed as a raw material for FPCBs. FCCL fabricated by sputtering has advantages in terms of its fine pitch etching and dimensional accuracy compared to casting or laminating type FCCL. FCCL is a system which brings together an electric conductor such as copper and an insulator such as polyimide (Noh et al 2010). Copper coated polyimide films are commonly used as FPCBs in the electronic industry (Barlow et al 2002 and Kamiya et al 2007). The good adhesion between the metallic layer and the substrate in combination with the small foil thickness make FPCBs mechanically flexible. In addition, if polyimide (PI) is used for substrate material, the circuit board can operate at high temperatures. (Svedberg et al 2006).

1.2 REVIEW OF LITERATURE FOR POLYIMIDES

There are comprehensive reviews to deal with the basic synthesis and characterization aspects of homopolyimides, copolyimides and polyimide composites (Sillion 1989, Wilson et al 1990, Ghosh and Mittal 1996, McGrath et al 1999).
1.2.1 Polyimides

The first report of a homopolyimide in the literature arose from the work of Bogert and Renshaw (1908). They discovered that 4-aminophthalic anhydride self-condensed to give an intractable polyimide. DuPont had successfully pioneered the invention of obtaining polyimides through reaction of soluble/processable intermediates known as poly(amic acid)s (Endrey 1966). Direct reaction of dianhydrides and aromatic diamines in the melt or in solution resulted in precipitation of intractable low molecular weight polyimidies (Sroog 1991, Ghosh and Mittal 1996). Kanakaraj and Kreutz (1994) synthesized homo and copolyimides, from the reaction of ODA with ODPA and ODPA/BTDA, for use as adhesives in making flexible multilayer polyimide metal-clad laminates in flexible printed circuits and tape automated bonding applications. Xua et al (2001) reported copolyimides with different chemical structure for xerographic photoreceptors and its electrophotographic properties. Vygodskii et al (2004) reported synthesis of polyimidies using ionic liquids as activating media for polycondensation processes. Kulkarni et al (2005) reported polyimidies and copolyimides having pendant benzoic acid moiety with high thermal stability and glass transition temperature between 260 and 330°C. Wang et al (2006) reported novel thermally stable polyimidies derived from pyridine bridged aromatic dianhydride and various diamines. Ye et al (2006) reported sulphonated polyimide copolymers from 1,4,5,8-naphthalenetetracarboxylic dianhydride, 4,4'-diaminostilbene-2,2'-disulfonic acid, and other three common diamines, i.e., 4,4'-oxydianilne, 4,4'-methylene dianiline, and 4,4'-(9-fluorenlylidene)-dianilne for fuel cell applications. Saeed and Zhan (2007) synthesized thermoplastic polyimidies derived from ODPA, BPDA and 3,4'-oxydianilne as adhesives for bonded joints. Jiang et al (2008) reported novel sulfur-containing fluorinated polyimidies, synthesized by the reaction of 2,2'-bis-(trifluoromethyl)-4,4'-diaminodiphenyl sulfide with different dianhydrides for
optical waveguide device. Chang et al (2011) reported the effects of backbone conformation on the surface morphology of the rubbed PI layer, the pretilt angle and surface energy of the alignment film.

1.2.2 Polyimide Composites

polyimide/silica–titania core-shell nanoparticle hybrid thin films from soluble fluorine-containing polyimide, colloidal silica, and titanium butoxide for anti-reflective coatings.

1.2.3 Polyimide Dielectrics

Polyimides are well known for their high temperature stability, good mechanical properties, excellent chemical stability, low thermal expansion coefficients and low dielectric constants. They have been widely used as interdielectric materials in microelectronics and large scale IC industry, as electrical insulations for conventional appliances, and as functional materials for other industrial applications.

Simpson and Clair (1997) developed low dielectric constant polyimides. The effect of polarizability, fluorine content, and free volume on dielectric constant was examined. In general, minimizing polarizability, maximizing free volume and fluorination all lowered dielectric constants in the polyimides studied. Maier (2001) reported low dielectric constant polyimides, heteroaromatic polymers, poly(aryl ether)s, fluoropolymers, hydrocarbon polymers without any polar groups, for microelectronics. Yang and Su (2003) reported the properties of organosoluble aromatic polyimides from 3'- trifluoromethyl-3,4'-oxydianiline and various dianhydrides with low dielectric constant between 2.8 and 3.5. Chen and Kang (2004) reported the synthesis of nanocomposites of polyimides with grafted methacrylate side chains containing polyhedral oligomeric silsesquioxane by thermally initiated free-radical graft copolymerization of methacrylcyclopentyl-polyhedral oligomeric silsesquioxane and ozone - preactivated poly(amic acid), followed by thermal imidization for dielectric applications. Watanabe et al (2005) synthesized nonfluorinated aromatic polyimides having dielectric constant as low as 2.74 using aromatic dianhydrides and an aromatic diamine containing phenylene ether units.
Lee et al (2005) synthesized novel polyimide hybrid nanocomposites containing polyhedral oligomeric silsesquioxane by copolymerization of octakis(glycidyldimethylsiloxy)octasilsesquioxane, 4,4'-oxydianiline diamine, and 4,4'-carbonyldiphthalic anhydride, to achieve the polyimide hybrid with lower dielectric constant and thermal expansion. They achieved dielectric constant to the extent of 2.65. Wang et al (2006a) synthesized polyimides derived from 2,6-bis[4-(3,4-dicarboxyphenoxy)benzoyl]pyridine dianhydride and different aromatic diamines with low dielectric constants. Chung and Hsiao (2008) showed that organosoluble fluorinated polyimides derived from 1,6-bis(4-amino-2-trifluoromethylphenoxy)naphthalene and aromatic dianhydrides had low dielectric constant between 2.75 and 3.13. Lin and Wang (2007) synthesized novel polyimide/mesoporous silica composites derived from pyromellitic dianhydride, 4,4'-oxydianiline and SBA-15 or SBA-16 with low dielectric constant between 2.61 and 2.73. Min et al (2008) synthesized functionalized SBA-15/polyimide derived from 2,2-bis(4-[aminophenoxy]phenyl)propane and ODPA with improved mechanical properties and low dielectric constant of about 2.6 at 1 MHz. Optically transparent fluorinated polyimides synthesized by Tao et al (2009) exhibited low dielectric constant of 2.49. Koytepe et al (2009) attempted a molecular-level design of low-dielectric constant material by embedding the nickelocene unit and by in situ curing of poly(amic acid) macromolecules. Polyimide/mesoporous silica hybrid nanocomposites synthesized by using PMDA and ODA based on water soluble poly(amic acid) ammonium salt had low dielectric constant up to 2.45 (Lee et al 2009). Hsiao et al (2010) reported that the highly soluble fluorinated polyimide derived from asymmetric diamine monomer containing flexible ether linkages and bulky trifluoromethyl substituents, namely 1,3-bis(4-amino-2-trifluoromethylphenoxy)naphthalene and aromatic dianhydrides exhibited low dielectric constant between 2.81 and 3.24 and high optical transparency. Babanzadeh et al (2010) reported synthesis of soluble thermally stable silane
containing aromatic polyimides with reduced dielectric constant. The dielectric constants of aromatic polyimides derived from 4,4′-diaminodiphenylmethane and 3,3′-dimethyl-4,4′-diaminodiphenylmethane with different dianhydrides were between 2.88 and 3.48. The cooperativity of the molecular motions associated with the relaxation processes was discussed (Chisca et al 2011). Park et al (2011) reported flexible photoresponsive organic field-effect transistor, phototransistor, based on a fluorinated copperphthalocyanine and polymer gate dielectric on a flexible polyimide substrate.

1.3 REVIEW OF LITERATURE FOR MESOPOROUS MOLECULAR SIEVES

The origin of mesoporous molecular sieves dates back to 1971 with the patent of Chiola et al (1971) who synthesised low density silica materials by the ammoniacal hydrolysis of tetraethylorthosilicate in the presence of cationic surfactant, alkyltrimethylammonium bromide. However these materials lacked attention due to incomplete characterisation results. It was when Renzo et al (1997) reproduced the above material resembling MCM-41 in its properties. Yanagisawa et al (1990) reported the synthesis of mesoporous materials through intercalation of cetyltrimethylammonium cations into the layered polysilicate kanemite followed by calcination to remove the organic species. The world-wide resurgence for new molecular sieves led Mobil researchers in the early 1990s to discover a new family of nanostructured mesoporous materials known as M41S. The three different phases in the family of M41S mesoporous molecular sieves are: hexagonal MCM-41 (Beck et al 1992), cubic MCM-48 (Vartuli et al 1994) and lamellar-MCM-50 (Dubios et al 1993). Among the three, MCM-41 is undoubtedly the best known and most widely studied material of this family. M41S materials are synthesised via a self-assembled liquid crystal mechanism involving sol-gel precursors in which growth of silica framework occurs
around cationic quarternary ammonium micelles, which act as surfactant in order to form a mesostructure in highly basic media. Figure 1.4 shows the three different arrays of M41S family. The successful discovery of M41S mesoporous molecular sieves largely intensified the focus on ordered mesoporous materials.

Figure 1.4  Schematic representations of three different arrays of M41S materials

1.3.1  Synthesis of Mesoporous Materials

Mesoporous materials form the backbone of many heterogeneous catalysts and separations media. Substantial efforts have led to unlock the hidden secrets of the mechanism of their formation. Much of the mechanistic work has focused on understanding the role of surfactants or templating agents which play a complex, cooperative role of spatial ordering through the filling of void space, balancing charge and stabilizing structural units. The organization of surfactant molecules into well ordered mesostructures plays a vital role in the formation mechanism of mesoporous materials. The phase behaviour of surfactants is a complex process that demonstrates the role of molecular structure on surfactant aggregation (Laughlin 1991 and Zana 1991). Two main path ways (1) cooperative self-assembly and (2) liquid-crystal templating processes seem to be effective in synthesising ordered mesostructures.
1.3.1.1 Synthesis of SBA-15

Zhao et al (1998) reported the synthesis of SBA-15 employing nonionic poly (alkylene oxide) block copolymers as the structure directing agent. Association of water molecules with the alkylene oxide moieties through hydrogen bonding causes the solubility of these surfactants in aqueous media. This can be increased by using highly concentrated acid where hydronium ions instead of water molecules are associated with the alkylene oxygen atoms.

Synthesis of mesoporous materials completely rely on surfactant micelles as templates for the assembly and subsequent condensation of inorganic precursors. The hydrogen-bonding interaction pathways were used to prepare mesoporous silica such as HMS (hexagonal mesoporous silica), SBA-15 (Santa Barbara Amorphous No. 15) and FDU-1 (Fudan University No. 1) with neutral non-ionic surfactants.

Zhao et al (1998) have prepared two-dimensional hexagonal material, SBA-15, with high surface area, large pore size and high wall thickness using a triblock copolymer viz., $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123) as the structure directing agent. Relative to MCM-41, SBA-15 materials possess higher hydrothermal stability. SBA-15 exhibits XRD pattern which can be indexed according to $\text{p6mm}$ space group with one intense peak (100) and few higher order small peaks (110, 200, 210 etc) at 2$\theta$ value below 10. The low temperature synthesis of large-pore SBA-15 silicas using tetramethyl orthosilicate as a silica source, Pluronic P123 (EO$_{20}$PO$_{70}$EO$_{20}$) triblock copolymer as a template, and 1,3,5-triisopropylbenzene as a micelle expander was reported by Liang and Michal (2010). These materials exhibited narrow pore size distributions and large pore volumes (above 1 cm$^3$ g$^{-1}$). Chareonpanich et al (2007) synthesized mesoporous silica SBA-15 from rice husk ash via the ultrasonic technique. It was shown to have higher specific
surface area, total pore volume, and microporosity than those prepared by the conventional technique in 24 h.

1.3.1.2 Synthesis of KIT-6

Kleitz et al (2003) for the first time reported the synthesis of a 3-D cubic mesoporous material named KIT-6 using Pluronic P123 (EO<sub>20</sub> PO<sub>70</sub> EO<sub>20</sub>) triblock copolymer as structure directing agent and TEOS as silica source in an aqueous medium with n-butanol as co-solute. Physico-chemical characterisation results of KIT-6 revealed the presence of large pore with thick wall, high specific surface area, pore volume and high hydrothermal stability. The structure of KIT-6 consists of interpenetrating bicontinuous network of channels such as those in MCM-48. In contrast to MCM-48, these two intertwined systems of relatively large channels in KIT-6 can also be connected through irregular micropores present in the mesopore walls analogous to those in SBA-15. Powder XRD patterns of these materials exhibit an intense peak at (211) and few higher order reflections at (220) and (332) that are indexed to Ia3d symmetry. Jo et al (2009) reported synthesis of high-quality KIT-6 mesoporous silica using water glass as a low-cost silica source.

1.4 PURPOSE OF THE PRESENT STUDY

Over the years, a tremendous amount of work has been performed on structure/property relationships in polyimides to obtain fundamental information that could be used to develop polyimides with a unique combination of properties for demanding applications (Hsiao and Chen 2002, Park et al 2004 and Pan et al 2007). Aromatic polyimides have inherently high tensile strength, modulus and flexibility in the film form depending on the molecular structure of the polymer chains (Khatua and Maiti 2002). In most of the studies, new aromatic dianhydrides and aromatic diamines were

The literature review presented earlier reveals that, much work has not been carried out in the synthesis of terpolyimides using different dianhydrides or diamines. The properties could be tailor-made with terpolyimides due to numerous possibilities to change the compositions of the monomers. Though a number of investigations has been undertaken to synthesize polyimides and copolyimides with excellent thermal, mechanical and chemical properties, their dielectric constant have been found to be between 3 and 4. In recent years the preparation of polyimides with still low dielectric constants and high performance has become one of the major research challenges for applications in microelectronics.

Several approaches were made to reduce the dielectric constants of polyimides which include (i) incorporation of fluorinated substituents into polyimide back bones (Madhra et al 2002, Miyagawa et al 2003, Myung et al 2004 and Li et al 2006), (ii) thermal degradation of the labile block or graft chains in the copolyimides (Chen et al 2004, Chen et al 2004a and Su et al 2005), and (iii) introduction of air gaps into interconnected structures and nanopores into polymers (Leu et al 2003 and Chen and Kang 2004 ). Considering that incorporation of air (dielectric constant =1), can reduce the dielectric constant remarkably by resulting in porous structure, most studies were focused on the last two approaches. Zhang et al (2005) incorporated hollow silica tubes into polyimide to reduce the dielectric constant. It has initiated interest for the use of mesoporous silicas to reduce the dielectric constant.
Hence in the present study, an attempt was made to synthesize and characterize terpolyimides by combining appropriate mole ratio of 3,3’4,4’-biphenyl tetracarboxylic dianhydride (BPDA); 3,3’,4,4’-benzophenone tetracarboxylic dianhydride (BTDA); 3,3’,4,4’-oxydiphthalic dianhydride (ODPA); 4,4’-hexafluoroisopropylidene bis(phthalic anhydride) (6FDA) and 4,4’-oxydianiline (ODA) for better thermal and mechanical properties, and low dielectric constant. Homo and copolyimides using the same monomers were also synthesized for comparison.

From the foregoing discussion it is evident that incorporation of fluorinated substituents or porous silica could reduce dielectric constant of polyimides. Moreover such studies were carried out with homo and copolyimides, but not with terpolyimides. So it was also planned to use the terpolyimide with good thermal and mechanical properties, and with low dielectric constant to fabricate mesoporous silica/terpolyimide nanocomposites by incorporating mesoporous silica to further reduce the dielectric constant.

Hence in the present study it was planned to exploit mesoporous materials such as SBA-15 and KIT-6 molecular sieves for the synthesis of mesoporous silica/terpolyimide nanocomposites with low dielectric constant. The choice of KIT-6 was based on the fact that, its pore diameter is larger than SBA-15, by which it can significantly reduce dielectric constant by entrapping more air. But SBA-15 and KIT-6 carry free uncondensed Si-OH groups (defective Si-OH groups), which should be completely masked, for example, by 3-aminopropyltriethoxysilane (APTS) functionalization, as they might increase dielectric constant.
1.4.1 Outline of the Present Investigation: Flow Chart

Figure 1.5 Outline of the present investigation

\[\text{TP1, TP2, TP3}^a\] BPDA/BTDGA/ODPA-ODA
\[\text{BPDA/BTDGA/6FDA-ODA}^b\] BPDA/BTDGA/6FDA-ODA

\[^a\text{TP1 - (BPDA/BTDGA/ODPA-ODA, 0.5:0.25:0.25::1)}\]
\[^b\text{TP4 - (BPDA/BTDGA/6FDA-ODA, 0.5:0.25:0.25::1)}\]

\[^a\text{TP2 - (BPDA/BTDGA/ODPA-ODA, 0.25:0.5:0.25::1)}\]
\[^b\text{TP5 - (BPDA/BTDGA/6FDA-ODA, 0.25:0.5:0.25::1)}\]
\[^b\text{TP6 - (BPDA/BTDGA/6FDA-ODA, 0.25:0.25:0.5::1)}\]
1.4.2 Scope of the Present Investigation

The scope of the study was as follows:

1st part of the study

- Synthesis of poly(amic acid)s (PAA) of
  (i) BPDA-ODA,
  (ii) BTDA-ODA and
  (iii) ODPA-ODA
  by the reaction of ODA with their respective dianhydrides in DMAc in the nitrogen atmosphere.

- Synthesis of co(polyamic acid)s of
  (i) BPDA/BTDA-ODA,
  (ii) BPDA/ODPA-ODA and
  (iv) BTDA/ODPA-ODA
  by the reaction of dianhydrides and ODA in the mole ratio 0.5:0.5:1 in the nitrogen atmosphere.

- Synthesis of ter(polyamic acid)s of BPDA/BTDA/ODPA-ODA by
  the reaction of dianhydrides and ODA in the mole ratio of 0.5:0.25:0.25:1, 0.25:0.5:0.25:1 and 0.25:0.25:0.5:1 in the nitrogen atmosphere.

- Thermal imidisation of the above poly(amic-acid)s by stage curing for 30 min each at 100, 150 and 200, and 6h at 250°C at a heating rate of 100°C/h.

- Characterisation of the above homo, co and terpolyimide films using FT-IR, TGA, DSC, tensile strength, tensile modulus and percentage elongation, dielectric constant and XRD.
2nd part of the study

- Same methodology was used to prepare and characterize copolyimides (BPDA/6FDA-ODA) and terpolyimides (BPDA/BTDA/6FDA-ODA). Homopolyimide BPDA-ODA and copolyimide BPDA-BTDA-ODA of the previous study were used for comparison.

3rd part of the study

- Comparison of thermal and mechanical properties, and dielectric constants of terpolyimides of BPDA/BTDA/ODPA-ODA and BPDA/BTDA/6FDA-ODA.

- Selection of the terpolyimide with high thermal and mechanical properties, and low dielectric constant.

- Hydrothermal synthesis of SBA-15 using tetraethylorthosilicate (TEOS) as the silicon source and P123 triblock copolymer as a structure directing agent.

- Hydrothermal synthesis of KIT-6 using TEOS as the silicon source and P123 triblock copolymer as a structure directing agent in the presence of n-butanol.

- Characterisation of them by FT-IR and TGA.

- Calcination of as-synthesized SBA-15 and KIT-6 at 550°C in air and characterisation of them by XRD, FT-IR, TGA, BET and SEM.

- Amino functionalization of SBA-15 and KIT-6 using APTS at 20% loading to obtain APTS-SBA-15 and APTS-KIT-6, and characterisation of them by XRD, FT-IR,TGA, BET and SEM.
Synthesis of terpoly(amic-acid) nanocomposite by the reaction of BPDA, BTDA, ODPA and ODA in the mole ratio of 0.5:0.25:0.25::1 with APTS-SBA-15 or APTS-KIT-6 at 2,4,6,8 and 10% loadings in DMAc in the nitrogen atmosphere.

Thermal imidisation of the above poly(amic-acid) nanocomposites by stage curing for 30min each at 100, 150, 200, 250°C, and 8 h at 300°C to obtain APTS-SBA-15/TPI and APTS-KIT-6/TPI nanocomposite films.

Characterisation of APTS-SBA-15/TPI and APTS-KIT-6/TPI nanocomposites by FT-IR, TGA, DSC, DMA, tensile strength, tensile modulus and percentage elongation, dielectric constant and SEM.