SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF NOVEL FLUORINATED POLY(IMIDE SILOXANE) COPOLYMERS

Thesis submitted to the Indian Institute of Technology, Kharagpur For the award of the Degree

of

Doctor of Philosophy

By

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Under the guidance of

Dr. Susanta Banerjee





MATERIALS SCIENCE CENTRE INDIAN INSTITUTE OF TECHNOLOGY, KHARAGPUR OCTOBER – 2008

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CERTIFICATE OF APPROVAL

29/12/2008

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Date: 30/10/2008



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DECLARATION

I certify that

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Anindita Ghesh. (Anindita Ghosh)

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IIT Kharagpur, October 2008

Aninclita Ghosh. Anindita Ghosh

Abbreviations and symbols

AFM	Atomic Force Microscopy
6FDA	4,4'-(Hexafluoro-isopropylidene)diphthalic anhydride
BPADA	4,4'-(4,4'-Isopropylidenediphenoxy)bis(phthalic anhydride)/ Bisphenol-A- di(phthalic anhydride)
BTDA	3,3'4,4'- Benzophenone tetracarboxylic acid dianhydride
COSY	Correlation Spectroscopy
dL /g	Decillitre per gram
DCM	Dicholoromethane
DDS	4, 4'- Diaminodiphenyl sulfone
DMA	Dynamic mechanical analyzer
DMAc	N, N- dimethyl acetamide
DMF	N, N- dimethylformamide
DMSO	Dimethyl sulphoxide
DSC	Differential scanning calorimeter
E	Dielectric constant
E″	Storage modulus
EB	Elongation at break
GPa	Giga Pascal
GPC	Gel permeation chromatography
ILD	Inter layer dielectric
IMD	Inter metal dielectric
IR	Infrared
KHz	Kilo hertz
M _n	Number average molecular weight
MPa	Mega Pascal
$M_{\rm w}$	Weight average molecular weight
NMP	n-Methyl pyrrolidone
NMR	Nuclear magnetic resonance

ODA	4,4'-oxydianiline
ODPA	4,4'-oxydiphthalic anhydride/ o-Diphthalic anhydride
PAA	Polyamic acid
PDI	Polydispersity index, M _w /M _n
PDMS	Aminopropylterminated polydimethyl siloxane
PEI	Poly(ether imide)
PI	Polyimide
PL	Photoluminescence
PMDA	Benzene-1,2,4,5-tetracarboxylic dianhydride / Pyromellitic dianhydride
T _d	Weight loss temperature / Decomposition temperature
T _g	Glass transition temperature
TGA	Thermogravimetric analyzer
	Tetrahydrofuran
TS	Tensile strength
UV	Ultraviolet
YM	Young's Modulus
wt	weight percentage

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Abstract

Polyimides with excellent thermal stability, chemical resistance, mechanical and electrical properties suffer from insolubility and intractability which cause difficulties in both synthesis and processing. Therefore, much effort has been devoted to synthesize tractable, processable polyimides by incorporation of flexible linkages, bulky substitutents and incorporation of $-CF_3$ groups within the polymer backbone. Polyimides with siloxane segment in the polymer backbone are reported to have enhanced solubility and processability, reduced moisture uptake, resistance to atomic oxygen and modified surface properties. Hence, in the present investigation both $-CF_3$ and siloxane segments were incorporated in the polyimide backbone to improve the solubility, processability and reduce water uptake and dielectric constant for high performance applications.

Accordingly, several new polymers were synthesized by the reaction of odiphthalic anhydride (ODPA) with four different diamines namely 4,4'-bis(*p*aminophenoxy-3,3"-trifluoromethyl)terphenyl,4,4'-bis(3"-trifluoromethyl-*p*-amino

biphenylether)biphenyl, 2,6-bis(3'-trifluoromethyl-p-aminobiphenyl ether)pyridine and 2,5-bis(3'-trifluoromethyl-p-aminobiphenylether)thiopene respectively each incorporated with 40 wt% of amino-propyl terminated polydimethylsiloxane (APPS) to yield novel poly(imide siloxane)s. However, decreasing the siloxane loading to 20 wt% caused solubility problem in casting films and hence dianhydride system was changed to bisphenol-A-di(phthalic anhydride)(BPADA) leading to successful synthesis of poly(imide siloxane)s with 20 wt% siloxane loading and thermal, mechanical and dielectric properties were thoroughly studied. Tailoring of thermal, mechanical and dielectric properties of the poly(imide siloxane)s were done by varying the siloxane loading from 5 - 40 wt% by using the same dianhydride namely BPADA and with the fluorinated diamine namely 4,4'-bis(3"-trifluoromethyl-p-aminobiphenyl ether)biphenyl. Segmented block copoly(imide siloxane)s were prepared and the variation of block length towards the physical properties of the resulting polymers were investigated. This study suggested that properties of this class of polymers can be tailored simply by varying the hard and soft block lengths for a definite siloxane loading contrary to different amount of siloxane loading in random copolymers.

Five new poly(ether imide)s and poly(imide siloxane)s were also synthesized from a new diamine monomer TFAA with commercially available dianhydrides namely PMDA, 6FDA, BTDA, ODPA and BPADA. Thorough investigations on thermal, mechanical, optical and dielectric properties were also studied of this series of polymers.

Keywords: Poly(imide siloxane)s, Solubility, Thermal properties, Mechanical properties, Dielectric properties.

Contribution made by the Author

A. Contribution in Refereed Journals from Thesis

[1] Ghosh, A. and Banerjee, S. (2008), Synthesis, characterization and comparison of properties of novel fluorinated poly (imide siloxane) copolymers, J. Appl. Polym. Sci., 107, 1831.

[2] Ghosh, A. and Banerjee, S. (2008), Synthesis, characterization and comparison of properties of novel fluorinated polyimides derived from bisphenol -A- dianhydride, J. Macromol. Sci., Part A: Pure and Appl. Chem., 45, 578.

[3] Ghosh, A. and Banerjee, S. (2008), Synthesis and characterization of novel fluorinated polyimides derived from 9, 10-bis [3'-trifluoromethyl-4'(4"-aminobenzoxy) benzyl]anthracene, High Perform. Polym., DOI: 10.1177/0954008308090259.

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B. Contribution in Refereed Journals outside the scope of the Thesis

[1] Salunke, A. K., **Ghosh, A.** and Banerjee, S. (2007), Synthesis and characterization of novel poly(arylene ether)s based on 9, 10 bis-(4-fluoro-3-trifluoromethylphenyl) anthracene and 2, 7 bis-(4-fluoro-3-trifluoromethylphenyl) fluorine, J. Appl. Polym. Sci., 106, 664.

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C. Conference Presentations

[1] Ghosh, A. and Banerjee, S. (2006), Preparation and characterization of novel aromatic polyimide-polydimethylsiloxane random copolymer, Emerging Trends in Polymer Science and Technology, 8-9th Sep, Indian Institute of Technology, Kharagpur.

[2] Digal, A. K., **Ghosh, A.** and Banerjee, S. (2006), Synthesis of novel hyperbranched polyimide, Emerging Trends in Polymer Science and Technology held in 8-9th Sep., Indian Institute of Technology, Kharagpur.

[3] **Ghosh, A.** and Banerjee, S. (2007), Fluorinated poly (imide siloxane) copolymers: synthesis characterization and properties, Young Scientists' Colloquium -07, 27th July, Meghnad Saha Auditorium, Rashbehari Shiksha Prangan, University of Calcutta, 92, A.P.C. Road, Kolkata - 700 009.

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1.1 Introduction

Aromatic polyimides were developed in the early 1960s and since then have been great technological importance due to their outstanding thermal, mechanical and electrical properties [1,2]. However, their applications have been limited in many fields because aromatic polyimides are normally insoluble in common organic solvents and have extremely high glass transition or-melting temperatures, which preclude melt processability. Hence, one of the drawbacks in using aromatic polyimides is their poor processability, and a great deal of effort has been made to improve the processing characteristics of these intractable polyimides [3,4]. One of the successful approaches to improve solubility and processability of polyimides with minimal detrimental effect on their high thermal stability is the introduction of flexible linkages along the backbones either in the diamine or in the dianhydride component. The flexible linkages [5-6] include ether, methylene, carbonyl, sulfur, sulfone, and isopropylidene as well as hexafluoroisopropylidene; bulky substitutents [7-8]; bulky units within the polymer backbone [9-11]; non - coplanar [12-13]; alicyclic monomers [14] or by disrupting the polymer chain via copolymerization. Polyimides containing ether linkages prepared through phenoxy derivatives via nitro displacements, especially General Electric's polyetherimide, Ultem [®]1000, have achieved great commercial success [15-16]. The insertion of fluorinated groups into the polyimide backbone allows to improve the solubility. This increased solubility is due to low cohesion energy provided by fluorinated groups, and particularly due to the reduction of charge transfer complex. On the other hand, the presence of fluorine increases the reactivity of the precursor dianhydrides [17]. One of the most interesting compromise between processability and thermal stability is given by imide siloxane copolymers[18-19]. These thermoplastic copolymers are melt processable and exibit good elastomeric properties. Because polyimide siloxanes are thermoplastic-segmented copolymers containing a siloxane segment along the backbone chain of the polyimide, these copolymers have several beneficial properties such as enhanced solubility, UV stability, resistance to degradation in aggressive oxygen environments, impact resistance, modified surface properties and a number of other interesting features such as good adhesion, low stress in thin film dielectrics, semiconducting polymer electrolytes, fire resistance, gas separation membranes and thermoplastic elastomeric applications. The literature review will focus on polyimide synthesis, difficulties encountered in processing aromatic polyimides, methods employed so far to overcome the difficulties, a brief review on poly(imide siloxane) copolymers followed by objectives and scope of the current thesis. A plan of work is arranged accordingly for improvement of properties by synthesizing new poly(imide siloxane) copolymers.

1.2 Polyimide synthesis

Polyimides are condensation polymers derived from organic diamines and organic tetracarboxylic acids (or derivatives). The two-step method consists of the formation of the poly(amic acid) precursor followed by cyclodehydration. The main synthetic techniques of polyimides formation are thermal imidization, solution imidization and chemical imidization. Scheme 1.1 shows the synthesis of Polyimide from Pyromellitic dianhydride and 4, 4'-oxydianiline (ODA).





1.2.1 Two step method via poly(amic acid)s

The reaction mechanism involve in this reaction is the nucleophilic attack of the amino group on the carbonyl carbon of the anhydride species. That results in opening of the anhydride ring to form an amic acid group. The resultant poly(amic acid) is then cyclized either thermally or chemically in a subsequent step to produce the desired polyimide. The formation of the poly(amic acid) is an equilibration reaction where the forward reaction is thought to start with the formation of a charge transfer complex between the dianhydride and the diamine[20]. The more electrophilic the dianhydride, the more susceptible it is to nucleophilic attack. The reactivity of the dianhydride monomer has been related to its electron affinity, higher values suggest greater reactivity of the dianhydride [21]. Strong electron withdrawing groups activate the anhydride for nucleophilic acyl attack on the anhydride carbonyl. The reactivity of the diamine is related to its basicity. The rate constants for imidization increase as the pKa of the protonated amine increases. Highly basic amines (e.g. aliphatic amines) may form salts during the initial stages of the reaction, upsetting the stoichiometry and preventing the attainment of high molecular weight. Solvent also play an important role in the reaction. The common solvents in poly(amic acid) preparation are dipolar aprotic solvents such as Dimethylsulfoxide (DMSO), dimethylacetamide (DMAc), dimethyl formamide (DMF) and methyl pyrollidinone (NMP) that can form strongly hydrogen bonded complexes with the carboxyl group that shift the equilibrium to amic acid side. As expected the reaction rate is generally faster in more basic solvents. Several other minor important side reactions concurrently proceed with the main reaction. This side reaction may become significant under certain conditions particularly when the main reaction is slow because of low monomer concentration and low monomer reactivity. The principal pathways involved in the formation of poly(amic acid) are as shown in Scheme 1.2.



Scheme 1.2: Major reaction pathways involved in poly(amic acid) synthesis

1.2.2 Thermal imidization of poly(amic acid)

The most common method of converting the poly(amic acid) to the polyimide is by bulk (or melt) imidization [22-24]. Films of the poly(amic acid)s are often cast from polar aprotic solvents and subsequently dried and imidized. This method is suitable for polyimides in the form of films, coatings and powders in order to allow the diffusion of byproducts and solvent without formation of voids in the final polyimide products. The problem of film cracking as a result of shrinking can be avoided by carefully controlling the curing profile. A typical heating schedule involves a stage below 150 °C, followed by a relative rapid temperature rise to a second stage above the glass transition temperature T_g of the resulting polyimides. The cast films are dried and heated gradually upto 250 – 350 °C depending on the stability and Tg of the polyimides. The imidization is accomplished through the nucleophilic attack of the amide nitrogen on the acid carbonyl carbon with elimination of water. The most solvent is slowly driven off in the first stage and imidization occurs in the second stage, where curing and shrinkage is reliable [25]. The heating cycle allows a conversion of poly(amic acid)s into corresponding imides of about 92-99% and that can be achieved via thermal imidization routes. Further heating at above 300 °C, cannot lead to 100% conversion because of the so called "kinetic interruption" effect [26]. It is noted that hydrolytically unstable residual amic acid units resulting from kinetic interruption are considered as defect sites and therefore complete imidization is more difficult to achieve.

1.2.3 High temperature solution imidization of poly(amic acid)

Poly(amic acid)s may also be imidized in solution. Cyclodehydration can be carried out at lower temperatures, and hence side reactions can be avoided resulting from high temperature imidization. Solution imidization offers a particularly attractive method since one pot syntheses to cyclized polyimides are possible [27]. The imidization process is affected by heating the poly(amic acid) at temperature as high as 180 °C in the presence of an azeotroping agent such as ortho dichlorobenzene, xylene or cyclohexyl pyrrolidone which is added to remove the water that is liberated during the reaction. Fresh solvent is also added time to time to make-up for the solvent loss.

1.2.4 Chemical imidization of poly(amic acid)

Poly(amic acid)s may also be chemically imidized. This is accomplished by using chemical dehydrating agents in combination with basic catalysts [28]. Various reagents have been employed including acetic anhydride, propionic anhydride, and n-butyric anhydride as dehydrating agents and pyridine, triethylamine and isoquinoline as basic catalysts.

1.3 Difficulties encountered in processing aromatic polyimides

The difficulties in processing conventional aromatic polyimides are due to the inherent molecular features of aromatic polyimides. Molecular stiffness, high polarity and high intermolecular association forces make these polymers virtually insoluble in any organic medium, and shift up the transition temperatures to well above the decomposition temperatures. Thus, the strategies to novel processable aromatic polyimides have focused on chemical modifications, mainly by preparing new monomers that provide less molecular order, torsional mobility and lower intermolecular bonding. Of the various alternatives to design novel processable polyimides, some general approaches universally adopted are: introduction of aliphatic or another kind of flexible segments which reduce chain stiffness, introduction of bulky side substituents which help for separation of polymer chains and hinder molecular packing and crystallization, use of enlarged monomers containing angular bonds which suppress coplanar structures, use of 1,3-substituted instead of 1,4-substituted monomers, and/or asymmetric monomers, which lower regularity and molecular ordering, preparation of co-polyimides from two or more

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dianhydrides or diamines. However, factors leading to better solubility or lower T_g or T_m in a polymer often conflict with other important requirements, such as mechanical properties, thermal resistance or chemical resistance. Therefore, an adjusted degree of modification should be applied to optimize the balance of properties.

1.3.1 Polyimides with aliphatic and other flexible spacers

Polyimides containing flexible spacers have gained importance as technical materials. Some segmented, fluorinated polyimides [29] and co-polyimides containing oligoethylene glycol sequences have been presented as processable polyimides with potential application as thermally stable adhesives and thermoplastics [30, 31]. Polyimides containing oligosiloxane segments are also included within this class of polyimides [32, 33]. Table 1.1 shows few examples of monomers containing flexibilizing spacer for polyimides.

Flexibilizing spacer	Monomer	Ref.
Perfluoroalkane sequence in dianhydride system	O O O O O O O O O O	29, 35
Oligoethylene glycol sequence in diamine system	H ₂ N-O-(CH ₂)n-O-NH ₂	31
Polysiloxane sequence in dianhydride system	CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	34
Polysiloxane sequence in diamine system	$\begin{array}{c} \begin{array}{c} CH_3 & CH_3 \\ H_2N \longrightarrow (CH_2)_3 & Si \longrightarrow O \longrightarrow Si \longrightarrow (CH_2)_3 & NH_2 \\ CH_3 & CH_3 \end{array}$	38, 39

Table 1.1: Monomers for polyimides containing flexibilizing spacers

The thermal stability of these segmented polyimides is dependant on their chemical structure and mainly on the flexible chain. Polyimides containing polyethylene glycol sequences are thermally unstable [37], whereas polysiloxane [33, 34], perfluoroalkanes

[35], and even alkanes [36, 37] provide a reasonable thermal stability. The combination of conventional and new monomers is providing an expansion of the scope to synthesize processable polyimides containing flexible spacers [38, 39]. Perfluoroalkylenes are the well acceptable groups to be introduced as flexibilizing moieties as they provide a substantial lowering of the T_g without greatly impairing the thermal, mechanical and chemical properties. Novel soluble and meltable aromatic polyimides containing flexible linkages have been developed to the growing demand of specific materials for advanced technologies. All of them are soluble in some specific organic media, showing glass transition temperatures in the range 250–380 °C.

1.3.2 Polyimides with bridging functional groups

Aromatic polyimides containing ketone or ether linkages in their repeating units either in the dianhydride or in the diamine give more tractable polyimides. The most important bonding linkages are -O-, C=O, -S-, -SO2-, -C(CH3)2-, -CH2-, -CHOH-, and - $C(CF_3)_2$ [40–45]. Table 1.2 shows few examples of polyimides from monomers with bridging functional groups in the main chain along with their glass transition temperatures. First, "kink" linkages between aromatic rings or between phthalic anhydride functions cause a breakdown of the planarity and an increase of the torsional mobility. Furthermore, the additional bonds lead to an enlargement of the repeating unit and, hence a separation of the imide rings take place whose relative density is actually responsible for the polymer tractability. The suppression of the coplanar structure is maximal when voluminous groups are introduced in the main chain, for instance sulforyl or hexafluoroisopropylydene groups, or when the monomers are enlarged by more than one flexible linkage. Hexafluoropropylidene, carbonyl and sulfonyl are the groups most advantageously incorporated concerning processability. This is due to the relatively large volume of these groups, and to the conformational characteristics imparted by them to the polymer chain. The poly(ether-imide), marketed under the trade name Ultem is amorphous, soluble polymer that show Tg values around 217 °C. They can be processed from the melt by conventional means, and offer a price-performance balance that enables them to compete successfully in the market of engineering thermoplastics.

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Bridging group	Polymer	Tg°C	Ref
SO ₂		300	40
0		370	42, 43
—C(CH ₃) ₂ —		297	44
C(CF ₃) ₂	$-N$ CF_3 CF	311	45

Table 1.2: Selected polyimides from monomers with flexible bridging group

1.3.3 Polyimides with bulky side substitutents

Soluble aromatic polyimides have also been carried out by introducing bulky substituents, aryl or heterocyclic rings. Rusanov *et al.* worked with pendent imide group leading to new soluble polyimides [46] containing phenyl pendent groups. The phenyl group does not introduce any relevant weakness regarding thermal stability, and provides a measure of molecular irregularity and separation of chains very beneficial in terms of free volume increase and lowering of the cohesive energy density [47-51]. Fluorene diamines and the so-called "cardo" monomers also mean valuable alternatives for the preparation of processable polyimides [52, 53]. On the other hand, the presence of the bulky side substituents in polyimides or in any other linear polymer causes a lowering of the chain's torsional mobility and generally an increment of the glass transition temperature [54, 55].

1.3.4 Polyimides with trifluoromethyl groups

The presence of trifluoromethyl groups and, in general, the substitution of fluorine for hydrogen, causes a dramatic change of properties. The combination of electronic and steric effects reduces the ability for interchain interactions and, particularly, hinders the formation of charge transfer complexes, which is a major factor of molecular packing and intractability in aromatic polyimides. Furthermore, the C-F bond is a high energy bond, so that polyimides containing fluorine are in general polymers with high T_g and excellent thermal properties, comparable to those of the conventional aromatic polyimides. They show some improved properties, such as

- low dielectric constant

- high optical transparency

- excellent mechanical properties

- low moisture absorption

- increased solubility

- low optical loss and low refractive index.

This excellent balance of properties has made fluorinated polyimides very attractive for some applications in advanced technologies, such as in high performance structural resins, thermally stable coatings and films, polymeric membranes for gas separation, polymeric waveguides, and other electronic and optoelectronic applications.

Matsuura *et al.* [56] reported a series of new fluorinated rigid-rod polyimides synthesized by the reaction of 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) [57], 2,2'-dimethyl-4,4'-diaminobiphenyl (DMDB) and 4,4'-diamino-*p*-terphenyl (DPTP) with 1,4-bis(trifluoromethyl)-2,3,5,6-benzenetetracarboxylic Dianhydride (P6FDA),1- (trifluoromethyl)-2,3,5,6-benzenetetracarboxylic dianhydride (P3FDA) and pyromellitic dianhydride (PMDA) and studied the properties of novel polyimides hence prepared. They were of the opinion that introduction of trifluoromethyl side chains into dianhydride units increases the (coefficient of thermal expansion) CTE but decreases the dielectric constant, the water absorption, the refractive index. Polyimides with trifluoromethyl side chains in the diamine unit have been observed to have higher CTEs and polymer decomposition temperatures than those with methyl side chains. On the other hand,

polyimides with trifluoromethyl side chains have lower intrinsic viscosities than those with methyl chains. The dielectric constant, the refractive index, and the water absorption rate was observed to decrease when the fluorine content was increased by introducing trifluoromethyl side groups into polyimide molecules



Figure 1.1: Chemical structures of dianhydrides and diamines ^[56]

Polymers are attractive for economical and practical optoelectronic devices and interconnections in optical communication systems. In particular, polymer optical waveguides have been investigated for use as flexible interconnections and in optoelectronic integrated circuits (OEICs). High thermal stability should have the first priority in optical waveguides used in OEICs in order to provide compatibility with high-performance IC fabrication processes. Precise control of the refractive index is essential for fabricating single-mode optical waveguides with core/cladding systems and for optical interconnections between different materials. Low optical loss in the near-infrared wavelengths of 1.3 and 1.55 pm is required. Matsuura *et al.* [58] measured the optical loss and refractive indices of fluorinated polyimides, 6FDA/TFDB, PMDA/TFDB, and their copolyimides at the visible and near-infrared wavelengths. The copolyimides being optically homogeneous did not show any optical loss through copolymerization.

Fluorinated polyimide 6FDA/TFDB showed low optical loss of 0.3 dB/cm at an optical telecommunication wavelength of 1.3 μ m.

Polyimides with a low dielectric constant, low water absorption and a low thermal expansion are very useful for interlayer dielectrics in electronic devices such as integrated circuits. Low dielectric constant polyimides and low water absorption polyimides were reported by several researchers [59-61]. A correlation of high free volume and low dielectric constant has been previously reported for polyimides [62, 63]. Positron lifetime spectroscopy and group additivity methods were used to quantify free volume fractions. The introduction of free volume in a polymer decreases the number of polarizable groups per unit volume resulting in lower values for ε_{atomic} and $\varepsilon_{dipolar}$. The addition of pendant groups, flexible bridging units, and bulky groups which limit chain packing density have all been used to enhance free volume in polyimides and are used in this study to examine their effect on dielectric constant. Although incorporation of fluorine into polyimides has been shown to lower dielectric constants, indiscriminate fluorine substitution may actually yield an undesired effect. Hougham et al. [64] have shown that non-symmetric substitution of fluorine for hydrogen increases the average magnitude of the dielectric constant by approximately 0.05 per substituted ring. Symmetric substitution of fluorine does not increase the net dipole moment of the polymer and hence, does not increase the dielectric constant. In fact, in the same study Hougham et al. have shown that the dielectric constant decreases with symmetric fluorine substitution by a combination of lower electronic polarizability and larger free volume. In this study, symmetric and nonsymmetric fluorinated groups are used to elucidate the influence of fluorine content on dielectric constant.

These properties have been observed in polyimides with trifluoromethyl groups introduced into the polymer backbone using 4,4'-(hexafluoro-isopropylidene)diphthalic anhydride and 6FDA monomers. The low thermal expansion polyimides were reported by Numata *et al.* [65].

Polyimides having excellent thermal stability have been investigated as waveguide materials. Optoelectronic applications require polyimides with low loss and high thermal stability. Reuter *et al.* [66] have reported the optical loss of commercial fluorinated

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polyimides containing hexafluoroisopropylidene $-C(CF_3)_2$ - groups and estimated the optical loss below 0.1 dB/cm at 0.63 µm using optimized conditions.

Aromatic polyimides find increasing use in the fabrication of multilayer interconnection systems [67]. However, aromatic polyimides absorb moisture [68] and they are insoluble in common organic solvents. One approach to solve these problems relies on the incorporation of flexible hexafluoroisopropylidene groups, $-(CF_3)_2C$ -, into the polymer chain [69]. Aromatic polyimides containing hexafluoroisopropylidene groups exhibit lower dielectric constants which are less sensitive to moisture than the conventional aromatic polyimides.

Hougham et al. [70] synthesized an appropriate series of polymers to facilitate the study of structure/property relationships of fluorine containing polyimides and to report some tentative generalizations derived from the results. The polymer series studied was essentially limited to those obtained from the 6F dianhydride because it proved to be the only dianhydride with which many of the fluorinated diamines namely 1.4 1,4-diamino-2-fluorobenzene (FPDA), 1,4 diaminobenzene (PDA), (trifluoromethyl)benzene diaminotetrafluorobenzene (TFPDA), 1.4-diamino-2 (TFMPDA), 1,4-diamino-2,5-bis (trifluoromethy1)benzene (2TFMPDA), 2,5-diamino-4methyltoluene (2DAT), octafluorobenzidine (OFB), 2,2'-bis(trifluoromethyl) benzidine (2, 2' PFMB), 3, 3'-bis(trifluoromethy1)benzidine (3, 3' PFMB) would form polymer films suitable for physical characterization. Table 1.3 shows the fluorinated polyimides and their repeat unit structures with the respective dielectric constants measured at 1KHz. Diamines with fluorinated groups in the position ortho to the amino groups were successfully polymerized to high molecular weight. It was found that fluorine substitution generally reduced the refractive index and dielectric constant, the latter more strongly in cases with symmetric substitution. It was estimated that around 50% of the observed decreasing trend in the dielectric constant versus percent fluorine can be attributed to a reduction in the absorbed moisture due to an increase in hydrophobicity. The remaining 50% can be apportioned, on average, between increased free volume (~25%) and reduced total polarizability (~25%). Little effect of fluorine substitution on dynamic thermal or thermo oxidative stability was observed for the series.
Polymer	Structure	ε _{1 KHz} (dry)
6FDA – PDA		2.81±0.024
6FDA – FPDA		2.85±0.041
6FDA – TFPDA	$-\bigvee_{O}^{O} \xrightarrow{CF_{3}} \xrightarrow{O} \xrightarrow{F} \xrightarrow{F}$	2.75±0.023
6FDA – TFMPDA	$-N$ CF_3 O CF_3 O CF_3 O	2.72±0.005
6FDA – DAT		2.74±0.039
6FDA – 2TFMPDA	$-N \rightarrow CF_{3} \rightarrow CF_{3$	2.59±0.030
6FDA – 2DAT	$-\underset{O}{\overset{O}{\longrightarrow}} \underbrace{\underset{CF_{3}}{\overset{CF_{3}}{\longrightarrow}}} \underbrace{\underset{O}{\overset{O}{\longrightarrow}}}_{O} \underbrace{\underset{CF_{3}}{\overset{O}{\longrightarrow}}} \underbrace{\underset{O}{\overset{O}{\longrightarrow}}}_{O} \underbrace{\underset{CH_{3}}{\overset{CH_{3}}{\longrightarrow}}}$	2.68±0.046
6FDA – OFB	$-N \xrightarrow{CF_3} CF_3 \xrightarrow{O} \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} \xrightarrow{F} F$	2.55±0.020
6FDA – 2,2' PFMB	$ \sum_{O}^{O} + \sum_{CF_3}^{CF_3} + O + \sum_{O}^{O} + CF_2 + O + O + O + O + O + O + O + O + O + $	2.715±0.035
6FDA – 33' PFMB	$ \begin{array}{c} 0 \\ N \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0$	2.582±0.009

 Table 1.3: Fluorinated copolymers and their repeat unit structures
 [70]

Feiring et al. [71] was of the opinion that a further improvement in polyimide properties might be achieved by replacing the trifluoromethyl groups in 2, 2'-bis (trifluoromethyl)benzidine (TFMB) with trifluoromethoxy substituents. The trifluoromethoxy group is chemically and thermally very stable [72] and is significantly less electron withdrawing than trifluoromethyl, [73] so the diamine should be more reactive in condensation polymerization. They bis have prepared (trifluoromethoxy)benzidine (TFMOB), as well as analogs 4.4'-djamino-2.2'-bis(1,1,2,2tetrafluoroethoxy)biphenyl (TFEOB) and 4,4'-diamino-2,2'-bis[2-(heptafluoropropoxy)-1,1,2-trifluoroethoxy]biphenyl (DFPOB) having larger fluoroakyl substituents. These novel diamines have been used with the stiff dianhydrides 9.9-bis-(trifluoromethyl)xanthene-2,3,6,7-tetracarboxylic dianhydride (6FCDA), 9-phenyl-9-(trifluoromethyl)xanthene-2,3,6,7-tetracarboxylic dianhydride (3FCDA), 3,3',4,4'biphenyltetracarboxylic dianhydride (BPDA) and pyromellitic dianhydride (PMDA) to make several new polyimides whose properties can be compared to those of polyimides from TFMB.



Figure 1.2: Structures of diamines and dianhydrides^[71]

High-quality polyimide films from these diamines have been prepared by standard procedures and their thermal, mechanical, and electrical properties compared to known polyimides, including those derived from 2, 2'-bis (trifluoromethyl)benzidine. A series of three new 2, 2'-fluoroalkoxy-substituted-4, 4'-benzidines were prepared. Polymers from the diamine with -OCF₃ substituents show an especially favorable combination of low

dielectric constant, moisture absorption, and coefficient of thermal expansion (CTE) and high thermal stability, suggesting promise as a next-generation material for electronics applications. Polymers from diamines with the largest fluoroalkoxy substitutents have very low moisture absorption, but surprisingly high CTE.

Polyimides based on these materials were shown to have valuable properties for electronics applications such as low moisture absorption, low dielectric constant, and low thermal expansion coefficient.

1.3.5 Poly(ether imide)s with trifluoromethyl groups

It is well known that the incorporation of fluorinated substituents into polymers decreases the dielectric constant due to the small dipole and low polarizability of the C-F bond. The free volume can be increased by replacement of methyl groups by trifluoromethyl groups. Thus fluorinated polyimides were developed in order to decrease the dielectric constant. Banerjee *et al.* [74-79] have incorporated both trifluoromethyl groups (CF_3) as well as ether linkages in the polyimide backbone by designing new diamine monomers. The presence of ether linkage broke the planarity and improved the mobility which ultimately leads to improvement in solubility in not only aprotic solvents but also to some extent in protic solvents too. Furthermore a reduced dielectric constant and low moisture uptake, high gas permeability and high optical transparency was also observed in these type of fluorinated poly(ether imide)s.

1.4 Poly(imide siloxane)s

Incorporation of siloxane oligomeric segments into a polyimide backbone yields soluble processable poly(imide siloxane) copolymers with a variety of good property characteristics. Although some thermal and thermooxidative stability is compromised through introduction of the siloxane segment, a number of improvements are also observed in processability, toughness, flexibility and in electrical properties.

1.4.1 General properties of polysiloxanes

- Increase solubility and processability
- Impart impact resistance
- Biocompatibility

- High water repellency (hydrophobic)
- Low dielectric constant, thermo-oxidative resistance
- Good adhesion properties to the substrate
- Low dielectric constant

1.4.2 Review of the earlier work on poly(imide siloxane)

Kuckertz [80] was the first to report poly (imide siloxane), in the year 1966 on reacting with pyromellitic dianhydride (PMDA) with an amine terminated siloxane dimmer to form the poly(amic acid) precursors followed by curing to yield the imide. Efforts at NASA Langley were made by St. Clair et al. in the early 1980 [81, 82] and by McGrath et al. [83-87] on block copolymers comprising of polydimethyl siloxane and polyimides. PDMS containing polyimide copolymers yield segmented or multiblock copolymers. The architecture influences the elastomeric behaviour, melt rheology and toughness in rigid materials. Two types of poly(imide siloxane) copolymers are generally prepared namely randomly segmented copolymers and perfectly alternating segmented copolymers. The most common method followed for the preparation of randomly segmented poly(imide siloxane) copolymers involves the reaction of preformed amino propyl terminated polydimethylsiloxane with a dianhydride and diamine monomer [88, 89]. The resulting amic acid intermediate is cyclodehydrated either by thermal or high temperature solution imidization technique (discussed in section 1.2.2 and 1.2.3). Perfectly alternating segmented copolymers are synthesized by polymerizing two different oligomers via reaction of their end groups. In this method the average block length of each segment is known before copolymerization.

Furukawa *et al.* [90] reported three series of thermoplastic polysiloxane-*block*polyimides were prepared from 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride, aromatic diamines with four phenylene rings and diamine-terminated polydimethylsiloxane. The tensile modulus of their films was lowered and the coefficient of thermal expansion was increased with increasing polysiloxane composition. The copolyimides showed a good adherence onto silicon wafer even without adhesion promoter added. The adherence was maintained even after exposure to an environment of 23 °C and 78% RH for 72h. The residual stress in the interface between the copolyimide

coating and the silicon wafer was lowered according to the tensile modulus of coating materials, so the introduction of polysiloxane into aromatic polyimides can afford excellent adhesion and stress relaxation properties despite mismatching in thermal expansion between polymer and substrate. Arnold et al. [91] tried to incorporate varying amount of respective amount of siloxane in the polyimide backbone, but incorporation has found to be less than that tried as determined by NMR techniques. In contrast investigation by Pechar et al. [92] have reported 22 and 41 wt% siloxane incorporation where they attempted 20 and 40 wt% incorporation respectively. In addition to increased solubility, slowly precapping the PDMS oligomer prevented premature chain extension. Sun et al. [93] reported a novel poly(imidesiloxane) of trade name (SIM-2000) used as spun-on dielectric which provided good high temperature stability at 450 °C. Kripotou et al. [94] investigated molecular mobility in relation to morphology in polyimidepoly(dimethylsiloxane) hybrid networks (PI-PDMS) by employing dielectric techniques. The modification of the siloxane segment did provide several desired improvements in the bulk and surface properties. Lai et al. [95-97] synthesized poly(imide siloxane)s from dianhydride (PMDA), 4,4'-oxydianiline (ODA), pyromellitic and oligomeric dimethylsiloxane (ODMS) and then utilized them in gas separation and pervaporation. Stern et al. [98] elucidated the structure / permeability relationships of silicone containing polyimides. They synthesized two types of polymers: one type synthesized from an aromatic dianhydride, an aromatic diamine and ODMS; and the other type synthesized from aromatic dianhydride containing a silicon atom and an aromatic diamine (silicone-modified polyimide). The gas permeability and selectivity of poly(imide siloxane) were rather similar to the silicone components characteristics than to those of polyimides. Jwo et al. [99] studied the dependence of the poly(imide siloxane)s on the solubility parameter of unmodified polyimides and the molecular weight and on the content of α, ω -bis(3-aminopropyl) polydimethylsiloxane.

Block copolymers are composed of two segments namely hard polymer segment and soft polymer segment which are arranged alternately. The distribution of small domains of the soft segment in the hard phase behave as toughened glassy polymers [100] while the distribution of the hard segments in the continuous soft segment give rise to thermoplastic elastomer [101]. It has been found from the literature that perfectly

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alternating segmented copolymers have a higher structural regularity and give better microphase separation with higher glass transition temperature and improved tensile strength compared to the randomly segmented copolymers [102].

Rogers [103] investigated the thermal properties of perfectly alternating and randomly segmented copolymers. The study revealed almost no difference between the T_g's of the copolymers with corresponding compositions which implied that the molecular weight of the imide segments was similar in the two materials. Incorporation of PDMS in the polyimide backbone leads to increase in hydrophobicity with increase in the value of water contact angle. Rogers [103] studied a series of ODPA-Bis P based poly(imide siloxane) block copolymers and reported a gradual lowering of thermal stability at 5% weight loss with increase in siloxane content. Variation of polyimide block length also influences the glass transition temperature (Tg). As the length of the polyimide block decreases the T_g also decreases [104]. This lowering of T_g is due to the partial phase mixing that occurs in the poly(imide siloxane) block interface[91]. Mechanical behavior also changes on incorporation of PDMS into the polyimide backbone. The poly(imide sioxane)s behave as toughened thermoplastics with high elongation at break compared to the homopolymers. Tesero et al. [105] reported that a 50% increase of fracture toughness values on incorporation of 5 wt% PDMS to the benzophenone tetracarboxylic acid - meta phenylene diamine (BTDA-MDA) based block copolymers. Morphological investigations carried out by various researchers [106, -108] indicated microphase separation of the poly(imide siloxane)s. Incorporation of 20 wt% siloxane loading exhibited a very fine microphase separated structure while a cocontinuous type morphology was observed on increasing the siloxane loading to 5 wt% [103].

1.5Objectives and scope

Aromatic polyimides synthesized from aromatic monomers exhibits excellent thermal, electrical and mechanical properties. Polyimides are often insoluble and intractable, in their fully imidized form, resulting in serious processing difficulties. Therefore, much effort has been spent on synthesizing tractable, processable polyimides that maintain reasonably high strength and environmental stability. In this respect, the incorporation of the flexible siloxane segments into the polyimide backbone structure can yield soluble, processable polyimides with good thermal and mechanical properties.

It is well known that incorporation of fluorine in the form of pendent trifluoromethyl (-CF₃) groups enhances fractional free volume which decreases the number of polarizable groups per unit volume, in turn limit chain packing density and hence increases solubility and processability. An additional positive effect of $-CF_3$ group is reduced moisture absorption due to non-polar character of the fluorocarbon group. In electronic packaging, low dielectric materials minimize cross talk and maximize signal propagation speed in devices. Hence, incorporation of fluorine in the form of $-CF_3$ groups decreases the dielectric constant due to small dipole moment and the low polarizability of the C-F bond. Additionally, solubility is also enhanced by incorporation of kinked linkage such as ether group (-O-) in the polyimide backbone which disrupts the planarity.

The polysiloxane component in poly(imide)s imparts a number of beneficial properties to the polymeric system including enhanced solubility, reduced water sorption and gas permeability, good thermal and ultraviolet stability, resistance to degradation in aggressive oxygen environments, impact resistance and modified surface properties. These particular advantages render polysiloxane – modified polyimides attractive for aerospace, microelectronics, gas separation and other high performance applications. Connection between siloxane segments and the polyimide is often achieved with aminopropyl silane linkers. Hydrophobic nature of the siloxane segments reduces water uptake and reduce dielectric constant.

Hence in the present study it is decided to incorporate fluorine in the form of trifluoromethyl group, ether and siloxane linkage in the polyimide backbone to yield highly soluble and processable poly(etherimide siloxane)s. A detailed investigation of their properties is carried out. Accordingly the following objectives are set for the present thesis.

Research objective # 1

To prepare new poly(ether imide)s with reasonable thermal stability and low dielectric constant.

Research objective # 2

Selection of anhydride to achieve better solubility.

Research objective # 3

Optimization of siloxane loading in terms of mechanical, thermal and electrical properties.

Research objective # 4

Preparation of segmented block copoly(ether imide)s and investigation of properties visà-vis variation of block lengths.

Research objective # 5

Preparation of new poly(ether imide siloxane)s containing anthracene moieties in the main chain.

1.6 Plan of work

To achieve the first objective poly(etherimide siloxane)s were synthesized by using dianhydride system as ODPA with four different laboratory synthesized diamines namely 4,4'-bis(p-aminophenoxy- 3,3"-trifluoromethyl) terphenyl, 4,4'-bis(3"-trifluoromethyl-paminobiphenyl ether)biphenyl, 2.6-bis(3'-trifluoromethyl-p-aminobiphenyl (3'-trifluoromethyl-*p*-aminobiphenylether)thiophene each ether)pyridine, 2.5-bis incorporated with 40 wt% of siloxane through amino propyl-terminated polydimethylsiloxane (APPS). Structural elucidation by FTIR, NMR techniques (¹H, ¹³C, ²⁹Si) and elemental analyses; thermal properties by DSC, DMA and TGA; mechanical properties and electrical properties were studied.

BPADA was selected as another anhydride to compare the properties with the polymers derived from ODPA and poly(ether imide)s were synthesized with the same laboratory synthesized diamines namely 4,4'-bis(*p*-aminophenoxy- 3,3"-trifluoromethyl) terphenyl, 4,4'-bis(3"-trifluoromethyl-*p*-aminobiphenyl ether)biphenyl, 2,6-bis(3'-trifluoromethyl-*p*-aminobiphenyl ether)pyridine, 2,5-bis (3'-trifluoromethyl-*p*-aminobiphenylether)thiopene each with 40 wt% siloxane and with further reduction of siloxane to 20 wt%. Structural characterization by FTIR, NMR techniques (¹H-NMR and ¹³C-NMR) and elemental analyses; thermal properties by DSC, DMA and TGA; mechanical properties and electrical properties were studied.

Optimization of thermal, mechanical and electrical properties were carried out by varying the siloxane loading from 5-40wt % with an interval of 5 wt% in the polymer

backbone using BPADA of dianhydride and 4,4'-bis(3"-trifluoromethyl-*p*-aminobiphenyl ether)biphenyl. Detailed characterization by FTIR, NMR techniques (¹H-NMR) and elemental analyses; thermal properties by DSC and TGA; mechanical properties and electrical properties were studied.

To achieve the fourth objective instead of random approach of preparation of poly(etherimide siloxane)s, block copoly(ether imide)s were synthesized by separately preparing hard block composed of dianhydride system as BPADA and 4,4'-bis(*p*-aminophenoxy- 3,3"-trifluoromethyl) terphenyl and soft block composed of BPADA as dianhydride system and amino-propyl terminated polydimethylsiloxane in two different pots and finally combining them after a definite time period resulting in block copoly(etherimide siloxane)s. The different block structures were generated for a said composition by creating different stoichiometric imbalance in two different pots by using Carother's equation.

A new diamine 9,10-bis[3'-trifluoromethyl-4'(4"-aminobenzoxy)benzyl]anthracene (TFAA) were synthesized and poly(ether imide) and poly(etherimide siloxane)s were prepared by utilizing commercially available PMDA, BTDA, 6FDA, ODPA and BPADA. A comprehensive characterization by FTIR, NMR techniques (¹H-NMR) and elemental analyses; thermal properties by DSC, DMA and TGA; mechanical properties and electrical properties were studied.

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CHAPTER 2

MATERIALS CHARACTERIZATION AND TECHNIQUES The details of the materials used and the experimental techniques followed in the present investigation are presented in this chapter.

2.1 Materials

2.1.1 Solvents

- Dichoromethane (E. Merck, India).
- > Dimethylacetamide (Spectrochem, India).
- ▷ N,N dimethylformamide (DMF) (E. Merck, India); DMF was purified by stirring with NaOH and distilled from P₂O₅.
- Methanol (Ranbaxy Fine Chemicals, India);
- N-methyl-2-pyrrolidone (NMP) (E. Merck, India); NMP was purified by stirring with NaOH and distilled from P₂O₅.
- Toluene (E. Merck, India);
- ➢ Hexane (E. Merck, India);
- Absolute Alcohol (Bengal Chemical & Pharmaceuticals Ltd., India);
- > Tetrahydrofuran (E. Merck, India);
- Ortho dichorobenzene (ODCB) (SISCO Research Laboratories Pvt. Ltd., India.

The solvents were purified and dried following the usual procedure[1, 2].

2.1.2 Chemicals

- Bisphenol A- diphthalic anhydride (BPADA); Aldrich, USA
- > o-Diphthalic anhydride (ODPA); Aldrich USA.
- > 4,4'-(Hexafluoro-isopropylidene)diphthalic anhydride (6FDA); Aldrich,USA
- > Pyromellitic dianhydride (PMDA); Aldrich, USA
- Benzophenone tetracarboxylic acid dianhydride (BTDA); Aldrich, USA
- ➢ 4-Amino phenol − E. Merck, India
- > 9,10-Dibromo anthracene –Aldrich, USA.
- Amino propyl terminated polydimethylsiloxane (APPS) Gelest Inc., USA The chemicals were used as received unless otherwise noted.

2.2 Characterization and testing methods

2.2.1 Elemental Analysis

The percentages of carbon, hydrogen and nitrogen were analyzed by pyrolysis method.

2.2.2 Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was used to examine the structure of the monomers and polymers. Spectra were obtained with Netzsch 870 FTIR Spectrophotometer instrument with KBr pellets, for the monomers. FTIR spectra of polymers were taken directly from thin films (10- $15\mu m$). The characteristic infrared absorption bands of aromatic ether and related compounds are given in Table 2.1

Groups	Absorption band (cm ⁻¹)	Intesity	Origin
Aromatic Imides	1780	S	C = O asym. stretch
	1720	Vs	C = O sym. stretch
	1380	S	C-N stretch
	725		C = O bending, imide deformation
Amic acids	2900-3200	М	COO-H and HN-H
	1710	S	C =O (COOH)
	1660	S	C = O (CONH)
	1550	M	C-NH
Anhydrides	1820	М	C = O
	1720	S	C = O
	720	S	$\mathbf{C} = \mathbf{O}$
Amines	~ 3200, 3400 (two bands)	W	NH_2 sym. Structure (s) NH_2 asym. Structure (s)
Siloxanes	1084, 1021	S	Si-O-Si stretching
	800	S	Si –C stretching

Table 2.1: Infrared absorption bands of imides and related compounds

2.2.3 Nuclear magnetic resonance (NMR) spectroscopy

¹H and ¹³C-NMR spectra [3] were referred to tetramethylsilane (TMS) at zero ppm. ¹H-NMR (500 MHz), ¹³C-NMR (100 MHz) were recorded on a Bruker 500 MHz instrument [reference zero ppm with TMS (¹H and ¹³C-NMR)]. ²⁹Si-NMR (300 MHz) was recorded on a Bruker 300 MHz instrument. Solvents used for ¹H-NMR / ¹³C-NMR / ²⁹Si-NMR were CDCl₃ or DMSO-d₆ depending on the solubility of the monomer/polymers in the particular solvent.

2.2.4 Solubility study

The solubilities of the polymers were investigated in different organic solvents such as NMP, DMF, THF, DMSO, DMAc, chloroform, dichloromethane and acetone by dissolving small amounts of each polymer in a test-tube and dissolving it in a minimum amount of particular solvent. It was attempted to obtain 10% (w/v) solution of all polymers in different solvents.

2.2. 5 Viscosity measurement

Viscosities of polymer solutions were determined by around 0.5 dL / g at 30 °C using Ubbelohde suspended level viscometer. The inherent viscosities as reported in the text were calculated using the following equation:

 $\eta_r = t_1 / t_0$ ----- (1)

 $\eta_{inh} = \ln \eta_r / C ----- (2)$

where, $t_1 =$ Time of flow for polymer solution.

 t_0 = Time flow for DMAc.

2.2.6 Gel permeation chromatography (GPC)

Molecular weights and molecular weight distributions of the polymers were determined by size exclusion chromatography (SEC) at ambient temperature using a Viscotek Gel Permeation Chromatography equipped with a VE 1122 solvent delivery system, a VE 3580 RI detector, and two Viscogel mixed bed columns (17392-GMHHRM), which were preceded by a guard column. Data analysis was collected using OmniSEC 4.2 software. THF was used as the eluent at a flow rate of 1.0 ml/min and calibration was carried out using low polydispersity poly (styrene) standards. Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity (M_w / M_n) were determined. For some of the samples gel permeation chromatography was performed in THF with a PL MIXED-C column (pore size 5µm) from Polymer Laboratories at a flow rate of 1.0 mL / min with linear polystyrene as a standard, using MALLS Detector from Wyatt Technologies. HPLC-Pump 64 from Knauer was used from this investigation.

2.2.7 Differential scanning calorimetry (DSC)

DSC measurements were made on a Netzsch DSC 200PC instrument, at a heating/ cooling rate of 20 °C / min in presence of nitrogen[4]. Pieces of polymer film

samples were kept in sealed aluminium pans and glass transition temperature (T_g) was taken at the middle of the step transition in the second heating run. DSC is a dominant technique for the thermal analytical investigation. It measures the difference in energy inputs into a substance and reference materials as they are subjected to a control temperature programme. For some of the samples DSC measurements were made on a DSC Q 1000 of TA Instruments at a scan rate of \pm 20 K/min under nitrogen.

2.2.8 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis of the thin film (0.1mm thick) was carried out on a TA Instrument DMA – 2980 (USA) under tension mode at a heating rate of 10 °C/ min at a frequency of 1Hz was used. The temperature dependence of storage modulus E', loss modulus E'' and loss tangent (tan δ) was measured from 40 °C to 250 °C. The maximum of the (tan δ) was used to determine the glass transition temperature of the polymer film samples. For some of the samples dynamic mechanical thermal analysis was performed on an Eplexor from GABO, Ahlden (Germany) under tension mode on thin film samples at a heating rate of 5 K / min and a frequency of 10 Hz.

2.2.9 Thermogravimetric analysis (TGA)

Thermogravimetry was carried out on a Netzsch TG 209F1 thermogravimetric analyser, at a heating rate of 10 °C/min. 8-10 mg sample was taken and decomposition temperature (T_d) of the polymer was studied under nitrogen and/or synthetic air depending on the purpose. Such analysis relies on a high degree of precision in three measurements: weight, temperature and temperature change. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues. For some of the samples thermal decomposition behavior of these polymers was investigated on a TGA Q 5000 of TA Instruments at a heating rate of 10 K / min under nitrogen.

2.2.10 Mechanical testing

Stress – strain behavior measurements of the polymer films such as tensile strength and elongation at break was investigated using H10KS – 0547 instrument under strain rate of 5% / min of the sample grip length. Rectangular shaped specimens

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were cut from the films. The tests were done with sample length 30mm and sample width of 10mm. Three samples were tested for each film for accuracy and the software identified the tensile strength and % elongation at break. Young's modulus was then calculated from Hooke's Law, [Young's Modulus = Longitudinal Stress / Longitudinal Strain]. For some of the samples the mechanical properties were estimated by tensile testing at 5 mm / min with a tensile tester Z010 from Zwick, Germany. The strain was measured optically with a Videoextensometer NG from Messphysik, Austria. Using gauge lengths of about 3 mm at 5 different positions of each specimen the maximal local strain was estimated.

2.2.11 UV – Visible spectra

Room temperature UV measurement was done using UV-vis spectrophotometer (Ocean Optics Inc., USA) consisting of detector, SD - 2000 and Source lamp DH – 2000. Polymer films were placed in front of the source lamp and measurement of Intensity vs Wavelegth (nm) was recorded by the software.

2.2.12 Photoluminescence spectra

Room temperature PL measurement was done using a pulsed xenon discharge lamp of 619 nm as the excitation wavelength in a Perkin- Elmer LS -55 system.

2.2.13 Water absorption study

Water absorption of the films was measured by using a Sartorius balance of sensitivity of 10^{-6} g. The dry films were immersed into double distilled water for 24 or 72 h at 30 °C. Weight gain by the film was taken into account to calculate water absorption.

% Water Absorption = $[(W - W_0) \times 100] / W_0$

where $W_0 =$ Initial weight of the film, and

W = weight of the water absorbed films

2.2.14 Measurement of dielectric constant

Dielectric constant of the polyimide films was measured by the parallel plate capacitor method with HIOKI 9700 LCR Hi Tester from 100 KHz to 1 MHz at a temperature 30 °C. For the thin films 0.1 mm was taken and it was kept between the parallel plates of a capacitor. The capacitance of the thin films was then measured. The values of capacitance and thickness of the thin films and the cross sectional area

of the parallel plates was then used to calculate the dielectric constant (ϵ) of the polymer [5].

 $\epsilon = \frac{\text{Capacitance}}{(8.854e^{-14} \text{ x Area of the film / thickness of the film)}}$

Where $\varepsilon =$ dielectric constant

2.2.15 Rheology

Rheology behavior of the films was studied by using AR-1000 Rheometer. Flow behavior of the polymer at a particular temperature and viscosity changes was noted with change in shear rate (1/s).

2.2.16 Atomic force spectroscopy

Atomic Force Microscopy (AFM) was studied by NT-MDT (Solver-Pro, Russia) in contact mode at room temperature.

2.2.17 Scanning electron spectroscopy

The morphology of the polymers was studied by using JSM – 6360 of JEOL Co. The square pieces of test specimen was carefully cut out from the test specimen and were auto sputtered coated with gold for the non – conducting nature of the polymer at 0° tilt angle for the morphological study.

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<u>CHAPTER 3</u>

GENERAL SYNTHESIS OF DIAMINO MONOMERS

3.1 Introduction

Fluorinated polyimides are of special interest because they render numerous high performance applications[1]. The search for new monomers is hence an interesting and important part of our current research. Incorporation of trifluoromethyl groups in the diamine monomers as reported earlier [2-4] serves to increase the free volume of the polyimides, thereby improving various properties such as solubility, electrical insulating properties without forfeiture of thermal stability [5]. These groups also tend to reduce water absorption [6], crystallinity and color [7] whereas they increase flame resistance, gas permeabilities [8] and optical transparency[9]. A novel diamine monomer 9, 10- bis (3"-trifluoromethyl-*p*-aminobiphenyl ether)anthracene (TFAA) is reported in this chapter.

3.2 General synthesis of diamino- monomers

The diamino monomers were prepared starting with compound 5- bromo-2-fluoro benzotrifluoride, as shown in Scheme 3.1. The dibromo compounds in each case together with toluene, aqueous Na₂CO₃ (1M), and Pd(PPh₃)₄ (3 mol % with respect to dibromo anthracene) were refluxed for 3 days, with vigorous stirring. The organic layer was separated and the aqueous phase was extracted with toluene. The combined organic layers were washed with excess water, dried over (MgSO₄) and concentrated. The concentrated organic layer was filtered over Al₂O₃ (type 100–125 mesh; activity 1, bed length 20 cm, and diameter 2 cm) to remove the catalyst Pd(PPh₃)₄. The column was washed with excess of toluene to obtain the desired product. Finally, each of the compounds [1,4-bis(2-fluoro benzotrifluoride)benzene [2]; 4,4'-bis(2-fluoro benzotrifluoride)biphenyl [3]; 2,6-bis (2-fluoro benzotrifluoride)pyridine [4]; 2,5-bis(2fluoro benzotrifluoride)thiophene [4] and 9,10-bis(2-fluoro benzotrifluoride)anthracene was obtained after removal of the toluene. The compounds were further purified by recrystallization from 1: 10 mixture of toluene / hexane. The final step of the synthesis of diamino monomers is a nucleophilic displacement of activated fluorine atoms of 1.4bis(2-fluoro benzotrifluoride)benzene; 4,4'-bis(2-fluoro benzotrifluoride biphenyl; 2,6bis(2-fluoro benzotrifluoride)pyridine; 2,5-bis (2-fluoro benzotrifluoride)thiophene and 9,10-bis(2-fluoro benzotrifluoride)anthracene with 4-amino phenol respectively. The reaction was carried out in NMP as solvent in the presence of excess of potassium carbonate as base. Toluene was used to remove the water formed in the acid-base reaction between phenol and base [10, 11]. The critical condition of this reaction is that the reaction temperature should not exceed 160 °C, and the reaction is to be performed under completely inert atmosphere.



Scheme 3.1 Synthesis of diamino monomers and their structures

The diamine monomers used: 4,4'-bis(*p*-aminophenoxy-3,3"-trifluoromethyl) terphenyl, 4,4'-bis(3"-trifluoromethyl-*p*-aminobiphenyl ether)biphenyl, 2,6-bis(3'-trifluoromethyl-*p*-aminobiphenyl ether)pyridine, 2,5-bis(3'-trifluoromethyl-*p*-aminobiphenylether)thiopene were prepared using the procedure reported in the previous articles [2-4]. A novel diamine TFAA anthracene has been synthesized using the procedure as shown in Scheme 3.1.

3.2.1 Synthesis of 9, 10- bis (3" - trifluoromethyl – *p*-aminobiphenyl ether) anthracene (TFAA)

Detailed synthesis of 9,10-bis(2-fluoro benzotrifluoride)anthracene is reported [12]. by 9,10-bis(2-fluoro previously TFAA synthesized weighing was benzotrifluoride)anthracene (4 g, 7.961 mmol), 4-amino phenol (2.172 g, 19.904 mmol) anhydrous K₂CO₃ (5.768 g, 41.798 mmol), NMP (20 mL) and toluene (100 mL) into a three-necked round-bottomed flask equipped with a stir bar, a dean stark trap fitted with a condenser and a nitrogen inlet. The reaction mixture was stirred at 130-140 °C (oil bath temperature) for 5 h, as water was removed azeotropically with toluene. The reaction temperature was increased to 160 °C and maintained for another 4 h. After cooling to room temperature the reaction mixture was added to a sufficient amount of water to precipitate an off-white solid which was collected by filtration and dried under vacuum at 80 °C overnight. Repeated recrystallization from ethanol / water (90:10) mixture afforded 9,10-bis (3"-trifluoromethyl-*p*-aminobiphenyl ether)anthracene as off-white fine crystals.



3.2.2 Characterization

Yield: 5 g (92%).

Melting point: 316.92 (DSC, heating rate 20 °C / minute).

Analytical calculation for $(C_{40}F_6O_2N_2H_{26})_n$ (680.662gmol ⁻¹)_n: C, 70.59; H, 3.85; N, 4.12. Found: C, 71.50; H, 3.51; N, 4.42.

IR (KBR) cm⁻¹: 3420, 3345 (-NH₂), 3062 (aromatic C-H), 1616 (C=C), 1156 (C-F), 1128 (C-O).



Figure 3.1: ¹H-NMR spectra of TFAA



Figure 3.2: ¹³C-NMR Spectra of TFAA

¹**H-NMR (DMSO-d₆):** δ (ppm) 7.74 (d, J = 10.5Hz, 2H, H5), 7.64 (d, J = 6Hz,H6, 2H, H11), 7.56 (d, J = 9Hz, 4H, H9,), 7.51-7.49 (m, 4H, H10), 7.11-7.09(m, 2H, H4), 7.00(d, J = 8.5Hz, 4H, H13), 6.70(d, J = 7.5Hz, 4H, H14), 5.15(s, 4H, H16).

¹³C-NMR (DMSO-d6): δ (ppm) 157.55(C3), 146.43(C12), 145.06(C15), 137.11(C7), 135.44(C6), 131.62(C11), 129.93(C9), 129.38(C2), 126.61(C8), 126.47(C10), 124.09(q, C1, J= 271.5Hz) 121.76 (C13), 118.68(C4), 117.51(C7), 115.50(C14).

3.3 Conclusion

A new diamine monomer TFAA was synthesized successfully. Elemental analysis values found by pyrolysis method showed very good matching of carbon, hydrogen and nitrogen percentages calculated theoretically. The formation of the diamino monomer was confirmed by FTIR spectroscopy which showed the required absorption bands. ¹H-NMR and ¹³C-NMR spectrum support the structure and ¹H-NMR spectrum showed very good matching of integrated peak areas for chemically different protons present in the diamino monomer. The diamine monomer was used to prepare several novel poly(ether imide)s and poly(imide siloxane)s with different dianhydrides discussed in Chapter 6A and Chapter 6B).

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CHAPTER 4

NOVEL FLUORINATED POLY(IMIDE SILOXANE)S FROM O-DI(PHTHALIC ANHYDRIDE)

4.1 Introduction

Polyimides with excellent thermal stability, chemical resistance, mechanical and electrical properties [1] suffer from insolubility and intractability which cause difficulties in both synthesis and processing. Therefore, the processing of the polyimides is carried out from soluble poly(amic acid) precursors, which are cast onto glass plates and converted to thin polyimide films by a rigorous thermal treatment. However, such process have certain limitations, including emission of volatile byproducts during curing and storage instability of the poly(amic acid) intermediate [2]. Therefore much effort has been spent to synthesize tractable, processable polyimides by incorporation of flexible linkages, bulky substitutents, and incorporation of $-CF_3$ groups within the polymer backbone. Behind all these approaches the main aim is to reduce polymer chain - chain interaction and reduce chain packing density.

Incorporation of pendant – CF_3 groups [3] into the polymer backbone enhanced the polymer solubility to some extent in organic solvents. However, the solution imidization was not very much successful as the polymer came out from the polymerizing solvent Hence, the work was further extended by incorporating flexible siloxane units to the previously reported homopolymer analogues [3] and four new poly(imide siloxane)s co-polymers was prepared by one pot solution imidization technique at 180° C reaction temperature in ortho-dichlorobenzene(ODCB) as solvent. Incorporation of flexible siloxane segment into the polyimide backbone enhances solubility and processability, reduce moisture uptake, show excellent atomic oxygen resistance and modified surface properties as reported earlier by many researchers [4-5].

4.2 Experimental

The experimental techniques used such as FTIR, ¹H-NMR, ¹³C-NMR, ²⁹Si – NMR, solubility study, GPC, DSC, DMA, TGA, mechanical properties (tensile stress, % elongation at break, Young's modulus), water absorption and dielectric properties and SEM are already discussed in Chapter 2.

4.3 General synthesis of poly(imide siloxane) copolymers from o-diphthalic anhydride

The polymers were made by the reaction of o-diphthalic anhydride (ODPA) with four different diamines namely 4,4'-bis(p-aminophenoxy-3,3"-trifluoromethyl)terphenyl, 4,4'-bis(3"-trifluoromethyl-p-aminobiphenyl ether)biphenyl, 2,6-bis(3'-trifluoromethyl-paminobiphenyl ether)pyridine, 2,5-bis (3'-trifluoromethyl-p-aminobiphenylether)thiopene respectively each with 40 wt% of amino-propyl terminated polydimethylsiloxane (APPS) as a co-monomer. The polymers are named as 1a40 wt% APPS, 1b40 wt% APPS, 1c40 wt% APPS and 1d_{40 wt% APPS} respectively. The reactions were conducted under constant flow of nitrogen. The polymerization procedure is shown in Scheme 4.1. Four reactions were carried out separately in 50 mL, 3 necked round - bottomed flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser charged with 0.605 g (1.95 mmol) ODPA, 0.59 g (1.024 mmol) of 4,4'-bis(p-aminophenoxy- 3,3"-trifluoromethyl) terphenyl and 0.80 g (0.926 mmol) APPS for the synthesis of poly(imide siloxane) $1a_{40}$ wt% APPS; 0.579 g (1.869 mmol) ODPA, 0.619 g (0.944 mmol) of 4,4'-bis(3"trifluoromethyl-p-aminobiphenyl ether)biphenyl and 0.80 g (0.925 mmol) APPS for the synthesis of poly(imide siloxane) 1b40 wt% APPS; 0.604 g (1.949 mmol) ODPA, 0.595 g (1.023 mmol) of 2,6-bis(3'-trifluoromethyl-p-aminobiphenyl ether)pyridine and 0.80 g (0.926 mmol) APPS for the synthesis of poly(imide siloxane) 1c40 wt% APPS and 0.602 g (1.943 mmol) ODPA, 0.597 g (1.018 mmol) of 2,5-bis (3'-trifluoromethyl-paminobiphenylether)thiopene and 0.80 g (0.925 mmol) APPS for the synthesis of poly(imide siloxane) 1d_{40 wt% APPS} each with 20 mL of 1,2-dichlorobenzene. The reactions were carried out under constant stirring and nitrogen flow. The temperature of the reaction medium was raised slowly from room temperature to 180 °C. During the course of reaction, the solutions were observed to turn viscous. The reactions were continued for 6 h at 180 °C. The resulting viscous polymeric solutions were cooled to room temperature and were precipitated from 500 mL methanol. The fibrous product obtained was dried and dissolved in 20 mL dichloromethane and re-precipitated from methanol. The products were dried at 120 °C for 5 h under vacuum and were used for further analysis. A weighed quantity of polymers was dissolved in a measured amount of dichloromethane (15 wt%) and was poured in flat bottom Petri dishes to obtain polymer

films. The Petri dishes were covered and the solvent was allowed to evaporate at a controlled rate at 30 °C overnight. The Petri dishes were then kept in a vacuum oven and the temperature of the oven was slowly raised to 120 °C and kept under continuous vacuum for 5-6 h to remove any trace of solvent.



Scheme 4.1: Reaction scheme and structures of $(1a - 1d)_{40 \text{ wt\% APPS}}$

4.4 Characterization

4.4.1 Poly(imide siloxane) - 1a_{40 wt% APPS}



Analytical calculation for $(C_{45.444}H_{50.533}F_{3.15}O_{10.472}N_2Si_{4.897})_n$, (989.75 g/mol)_n : C, 55.15; H, 5.15; N 2.83. Found: C, 56.26; H, 4.69; N, 3.11.
IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2961(-CH₃ group present in APPS); 1776 and 1720 (asymmetric and symmetric –CO- stretching); 1609 (C=C ring stretching); 1506, (band due to C-F absorption); 1388 (asymmetric C-O-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 8.04-7.13(15H), 3.69(s, 4H, -CH₂-N<), 1.68(s, 4H, -CH₂-), 0.56(s, 4H, -CH₂-Si), 0.33(m, 60H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.4, 166.2,161.4, 160.8, 156.2, 154.1, 138.5, 135.9, 134.9, 131.6, 131.2, 128.1, 127.5, 126.3, 124.8, 122.5, 120.4, 119.5, 114.0, 41.1, 22.5, 15.3, 1.7

4.4.2 Poly(imide siloxane) - 1b40 wt% APPS



Analytical calculation for $(C_{48.3669}H_{53.67}F_{3.03}O_{10.618}N_2Si_{5.103})_n$, $(1033.87 \text{ g/mol})_n$: C, 56.19; H, 5.23; N 2.71. Found: C, 56.56; H, 4.98; N, 2.98.

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2961(-CH₃ group present in APPS); 1775 and 1720 (asymmetric and symmetric –CO- stretching); 1610 (C=C ring stretching); 1506, (band due to C-F absorption); 1392 (asymmetric C-O-C stretching).

¹**H-NMR (CDCl₃):** δ (ppm) 8.05-7.14(17H), 3.66(s, 4H, -CH₂-N<), 1.70(s, 4H, -CH₂-), 0.57(s, 4H, -CH₂-Si), 0.27(m, 60H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.2, 166.2, 161.4, 160.5, 156.3, 154.0, 139.7, 138.2, 136.1, 134.5, 131.6, 128.0, 127.2, 126.2, 125.7, 124.8, 124.0, 120.4, 119.5, 113.9, 113.5, 41.0, 22.5, 15.3, 1.1.

4.4.3 Poly(imide siloxane) - 1c40 wt% APPS



Analytical calculation for $(C_{44,919}H_{50,008}F_{3,15}O_{10,472}N_{2.525}Si_{4.897})_n$, (990.27 g/mol)_n : C, 54.48; H, 5.09; N 3.57. Found: C, 55.02; H, 4.64; N, 3.82.

IR (KBR) (cm⁻¹): 3071(aromatic C-H stretching); 2961(-CH₃ group present in APPS); 1775 and 1720 (asymmetric and symmetric –CO- stretching); 1610 (C=C ring stretching); 1506, (band due to C-F absorption); 1392 (asymmetric C-O-C stretching).

¹**H-NMR (CDCl₃):** δ (ppm) 8.46-7.17(15H), 3.74(s, 4H, -CH₂-N<), 1.69(s, 4H, -CH₂-), 0.57(s, 4H, -CH₂-Si), 0.26(m, 60H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.3, 166.2, 161.4, 161.1, 160.8, 160.5, 156.0, 155.4, 154.9, 138.0, 135, 134.4, 131.7, 128.1, 127.2, 126.2, 124.2, 119.7, 118.7, 113.9,

41.0, 22.5, 15.3, 1.1.

4.4.4 Poly(imide siloxane) - 1d40 wt% APPS



Analytical calculation for $(C_{44,431}H_{49,541}F_{3,144}O_{10,479}N_2Si_{4,897}S_{0,524})_n$, (993.20 g/mol)_n : C, 53.71; H, 5.03; N 2.82. Found: C, 54.79; H, 4.65; N, 2.94.

IR (KBR) (cm⁻¹): 3071(aromatic C-H stretching); 2961(-CH₃ group present in APPS); 1776 and 1720 (asymmetric and symmetric –CO- stretching); 1610 (C=C ring stretching); 1499, (band due to C-F absorption); 1392 (asymmetric C-O-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 8.04-7.07(14H), 3.66 (s, 4H, -CH₂-N<), 1.69(s, 4H, -CH₂-), 0.57(s, 4H, -CH₂-Si), 0.27(m, 60H, Si-CH₃).

¹³C-NMR (CDCl₃): δ (ppm) 166.2, 161.4, 161.1, 160.5, 156.0, 154.0, 141.9, 134.5, 130.2, 129.6, 128.1, 126.2, 125.5, 124.8, 122.5, 122.1, 120.4, 119.5, 113.9, 41.0, 22.5, 15.3, 1.1

4.5 Results and discussions

4.5.1 FTIR spectroscopy

The formation of poly (imide siloxane)s were confirmed by FTIR spectroscopy. FTIR spectra of the polyimide films showed absorption bands at about 1780 cm⁻¹ (C=O asymmetric stretching) and 1730 cm⁻¹ (C=O symmetric stretching), corresponding to imide bands [6]. Absorption band at 2961 cm⁻¹ was due to the presence of methyl groups around APPS. No absorption band existed at 3400 cm⁻¹ corresponding to amide (-NH-) and acid (-OH) stretching and 1660 cm⁻¹ corresponding to amide (C=O) stretching indicating complete imidization.

4.5.2 ¹H- NMR spectroscopy

¹H-NMR spectra of the polymers did not show any amide or acid protons, indicating full imidization. The ¹H-NMR spectrum of poly (imide siloxane)s 1a_{40 wt% APPS} is shown in Figure 4.1 respectively. There is very good matching of integrated peak areas for different chemically different protons in all the four polymers.

The incorporation of siloxane in the polymers was calculated from the integrated peak areas of the proton NMR spectra. The gross molecular formula of the copolymers can be derived from the gross composition of the raw materials, e.g. for quadriphenyl unit containing polymer ($1b_{40 \text{ wt\% APPS}}$), the molecular formula of the copolymer can be presented as [-(APPS)_{0.505}-(ODPA)₁-(Quadri)_{0.495}]. Taking this molecular formula for copolymer $1a_{40 \text{ wt\% APPS}}$ the ratios calculated theoretically for the different aromatic protons contributed by the ODPA and quadriphenyl unit to the total aliphatic protons contributed by the APPS is 17.11: 36.56 while the ratio of aromatic protons to that of aliphatic protons found from integrated peak areas calculated from ¹H-NMR spectra (Figure 4.1) corresponds to 9.84:18.72. This corresponds to the 35.61% siloxane incorporation in polymer $1b_{40 \text{ wt\% APPS}}$. Similarly siloxane incorporation of polymers $1a_{40}$ wt% APPS, $1c_{40 \text{ wt\% APPS}}$ and $1d_{40 \text{ wt\% APPS}}$ were also calculated and presented in Table 4.1.

Polymer	C-aro	C-ali	F-aro	F-ali	C-ali/aro	F-ali/aro	A - Silo (%)
la _{40 wt} % APPS	15.45	35.08	37.8	77.69	2.270	2.055	36.208
1b40 wt% APPS	17.11	36.56	9.84	18.72	2.136	1.902	35.615
lc _{40 wt} % APPS	14.93	35.08	14.96	31.68	2.349	2.117	36.046
ld _{40 wt%} APPS	14.38	35.16	12.89	28.21	2.445	2.188	35.808

Table 4.1: Actual incorporation of siloxane in $(1a - 1d)_{40 \text{ wt\% APPS}}$ from ¹H-NMR spectra

C-ali = Theoretical number of aliphatic protons calculated from structure

C-aro = Theoretical number of aromatic protons calculated from structure

C (ali/aro) = Theoretical ratio of aliphatic/aromatic protons

F (ali/aro) = Found ratio of aliphatic/aromatic protons calculated from integrated peaks A-silo (%) = [F(ali/aro)/C(ali/aro)x 40] =Actual wt% incorporation of siloxane in the polymer structure.

Table 4.1 represents the number of aromatic and aliphatic protons calculated from the structures of poly (imide siloxane)s theoretically and their ratios and that found from integrated peak areas from proton NMR spectra. In each of the following cases it is observed from Table 4.1 that the ratio of aliphatic/aromatic protons found from the integrated peak areas is less than the calculated values from gross molecular structure. It is observed that though each of the poly(imide siloxane)s have been prepared with the view of incorporating 40 wt% siloxane loading, the actual incorporation found is around 36 wt% in all the four cases.



Figure 4.1: ¹H-NMR spectrum of poly(imide siloxane) 1b_{40 wt% APPS}

4.5.2.1 Calculation of siloxane loading from ¹H-NMR spectrum of 1b_{40 wt% APPS}

Referring to Figure 4.1 the following calculation has been done to find the actual siloxane incorporation in the polymer $1b_{40 \text{ wt\% APPS}}$.

Moles of ODPA = 1

Moles of aromatic diamine = 0.505

Moles of APPS = 0.495No. of aromatic protons = $22 \ge 0.505 + 6 \ge 1 = 17.11$ No. of aliphatic protons = $61.86 \ge 0.495 + 12 \ge 0.495 = 36.56$ Theoretical Ratio, C(ali/aro) = 2.136Total area under the aromatic region peaks = 9.84Total area under the aliphatic region peaks = 18.72Found Ratio calculated from integrated peaks, F(ali/aro) = 1.902Actual wt% incorporation of siloxane in the polymer structure = $(1.902/2.136) \ge 40 = 35.61$ For the other polymers, amount of siloxane incorporation was also calculated in a similar way.

4.5.3 ¹³C – NMR spectroscopy

The proton decoupled NMR spectra support the formation of the polymers. The ¹³C-NMR signals matches with the expected number of magnetically different carbons.

4.5.4²⁹ Si – NMR spectroscopy

In order to understand this less siloxane incorporation in the poly(imide siloxane)s, silicon NMR [29 Si – NMR] spectrum of the polymer 1b_{40wt% APPS} was recorded as shown in the Figure 4.2. For better understanding 29 Si-NMR of APPS was also recorded and is overlapped in the same figure.



Figure 4.2: ²⁹Si-NMR spectrum of 1b_{40 wt% APPS} overlapped with ²⁹Si-NMR of APPS

It is observed from the figure that ²⁹Si - NMR of APPS show two different silicone peaks at -28 and 8 ppm corresponding to the main chain –O-Si-O- and terminal –O-Si-Csignal connected to allyl amine which in turn corresponds to the integrated peak areas in a ratio of 8.3: 2. This indicates that the siloxane block length in APPS is 8.3. In case of the copolymer $1b_{40 \text{ wf% APPS}}$ (as shown overlapped in the same figure), the main chain –O-Si-O- reduces from 8.3 to 7.5; this indicates reduction in siloxane block length during polymerization. This may be due to amic acid catalyzed equilibration reaction; plausible mechanistic scenario for this amic-acid mediated siloxane equilibration reaction involves intermolecular catalysis by the amide-acid leading to siloxane cleavage. Thus less siloxane incorporation is not due to any relative reactivity or any kind of impurity related issues; rather it is a post amic acid formation phenomena and does not affect the polymer formation reaction vis-à-vis molecular weight development as indicated by GPC results reported in section 4.5.6 of this chapter. The siloxane incorporation calculated from silicon NMR for $1b_{40 \text{ wt\% APPS}}$ is $(7.5 / 8.3 \times 40) \sim 36.1 \text{ wt\%}$ which is in close agreement with the proton NMR data as shown in Table 4.1.

4.5.5 Polymer solubility

The solubilities of the resulting poly (imide siloxane)s were investigated in different organic solvents. Solubility behavior of the polymers in different solvents is presented in Table 4.2. These polymers exhibited very good solubility behavior in common organic solvents such as chloroform (CHCl₃), dichloromethane (CH₂Cl₂), Dimethylformamide (DMF), N, N-dimethyl acetamide (DMAc), and N-methyl-2-pyrrolidinone (NMP).

Table 4.2: Solubility characteristics of (1a – 1d) 40 wt% APPS

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	CH ₂ Cl ₂	Acetone
la _{40 wt} % APPS	+	+	+	-	+	+	+	-
1b _{40 wt} % APPS	+	+	+	-	+	+	+	-
1c _{40 wt} % APPS	+	+	+	-	+	+	+	-
1d _{40 wt} % APPS	+	+	+	-	+	+	+	-

+, soluble; -, insoluble at reflux

In comparison to the previously reported polymers [3] these polymers exhibited dramatic improvement in solubility. This is possibly due to the anchorage of siloxane moiety in the polymer backbone which increases the flexibility contributing to ease of the polymer to solvent attack.

4.5.6 Molecular weight determination of the polymers

Number average molecular weight (M_n) and polydispersity index (PDI) was determined by gel permeation chromatography. The molar masses of the poly (imide siloxane) reported in Table 4.3 indicate formation of high molar masses.

Polymers	η _{inh} (dL/g)	M _n	PDI	Film Quality
la40wt% APPS	0.32	24500	1.85	Clear, flexible
1b _{40wt} % APPS	0.39	32866	2.32	Clear, flexible
1c _{40wt} % APPS	0.45	41133	2.47	Clear, flexible
1d _{40wt%} APPS	0.41	33800	1.91	Clear, flexible

Table 4.3: Molecular weight and PDI of $(1a - 1d)_{40 \text{ wt\% APPS}}$

 $\eta_{inh} = 0.5$ weight % solution of poly(imide siloxane)s in DMAc at 30 °C $M_n =$ number average molecular weight PDI = polydispersity index

4.5.7 Glass transition temperature versus polymer structure

The poly (imide siloxane)s exhibited no crystallization or melting transition in DSC measurements. These polymers show glass transition temperature, which indicates amorphous or glassy morphology. DSC curves of the polymers are shown in Figure 4.3. The glass transition values are summarized in Table 4.4. The polymer $1b_{40 \text{ wt% APPS}}$ has been observed to exhibit highest T_g values than other polymers, which is due to the presence of rigid quadriphenyl unit in the backbone. The next higher glass transition temperature is observed in case of polymer $1a_{40 \text{ wt% APPS}}$ containing rigid terphenyl unit in the polymer backbone.



Figure 4.3: DSC plots of the poly (imide siloxane)s 1a40 wt% APPS and 1b40 wt% APPS

K				$ \begin{array}{c} CH_{3} \\ - CH_$	
	Polymers	Ar		T _g °C	
	1a _{40 wt} % APPS		242	172	
	1b40 wt% APPS	-0-0-	254	225	
	1c _{40 wt} % APPS	Â.	241	162	
	1d _{40 wt} % APPS	s↓	234	160	

Table 4.4: Glass transition temperature of $(1a - 1d)_{40 \text{ wt\% APPS}}$

[a] T_g 's of the homopolyimides without siloxane unit; taken from reference [3]

The following order of glass transition temperature is observed from Table 4.4; quadriphenyl > 1, 4 diphenyl benzene > 2, 6-diphenyl pyridine > 2, 5-diphenyl thiophene. This order could be explained on considering three factors: rigidity, catenation angle of different groups as shown in following scheme and the polarity.



Figure 4.4: Catenation angle of different arylene rings

Figure 4.4 shows the catenation angle of different arylene rings. A macromolecule exhibits more extended geometry (i.e., higher catenation angle providing by the different building blocks is expected to have higher glass transition temperature). Similarly, if the polymer molecule is built up of rigid units, it is expected to have higher glass transition temperature. The catenation angle between 1, 4'-diphenyl benzene and 4, 4' – diphenyl biphenyl units is the same that show, 180°; however, the polymer containing 4, 4' diphenyl biphenyl units exhibiting higher T_g is due to rigidity of this unit. The glass transition temperature of the polyimides containing pyridine and thiophene units in the polymer backbone shows a different behavior. A lowering in glass transition is observed

for the thiophene containing polymers than the pyridine containing polymers although the catenation angle for thiophene moiety is 148° which is higher than the pyridine moiety, 120°. This may be due to the polarity of the pyridine ring. Pyridine has more extended geometry than thiophene; at the same time pyridine has four times more polarity than thiophene ($\mu_{pyridine} = 7.4 \times 10^{-30}$ Cm; $\mu_{thiophene} = 1.83 \times 10^{-30}$ Cm) [7], which is the probable reason for higher T_g for pyridine ring containing polymers. It is also observed from Table 4.4 that the polymers 1a_{40 wt%} APPS, 1b_{40 wt%} APPS, 1c_{40 wt%} APPS and 1d_{40 wt%} APPS shows glass transition temperatures lower than those of the respective homo-polymers [3]. This is due to the incorporation of flexible siloxane units in the polyimide backbone which weakens the glass transition temperatures to some extent, indirectly indicating good microphase separation. It is also to be noted that the T_g of 1b_{40 wt%} APPS is higher than commercially available Ultem [®]1000 (T_g, 217 °C) based on bisphenol-A-diphthalic anhydride (BPADA) [8].

4.5.8 DMA measurements

The T_g 's taken from the tan ∂ peaks at 1Hz are given in Table 4.5. These values are comparable with the calorimetric T_g values. The polymers showed much lower storage modulus values in comparison to the analogous homo-polymers as reported earlier [3]. The polymer films showed storage modulus around 400 MPa at room temperature which gradually decreased with increase in temperature. The tan ∂ values show a maximum at a particular temperature, which in turn indicates the T_g 's of the polymers which are in good agreement with the T_g values obtained from DSC measurements.

Plots of the dynamic mechanical behavior of the polymer films $1a_{40 \text{ wt\% APPS}}$, $1b_{40 \text{ wt\% APPS}}$, $1c_{40 \text{ wt\% APPS}}$ and $1d_{40 \text{ wt\% APPS}}$ are shown in Figures 4.5 - 4.8 below.

Polymer	Storage modulus (MPa)	DMA (tan ∂)T _g (°C)
la40 wt% APPS	385	205
1b _{40 wt} % APPS	445	231
1c _{40 wt%} APPS	447	151
1d _{40 wt%} APPS	425	141

Table 4.5: Storage modulus and $\tan \partial$ of $(1a - 1d)_{40 \text{ wt\% APPS}}$



Figure 4.5: DMA plot of 1a40 wt% APPS



Figure 4.6: DMA plot of 1b40 wt% APPS



Figure 4.7: DMA plot of 1c40 wt% APPS



Figure 4.8: DMA plot of 1d_{40 wt%} APPS

4.5.9 Thermal stability

The thermal properties of the copolymers were evaluated by TGA. TGA curves of the polymers are shown in Figure 4.9. The thermal properties of the polymers are summarized in Table 4.6. The 5% weight loss under nitrogen of these polymers is in the temperature range of 434 - 460 °C while 50% weight loss is observed in the temperature range above 500 °C which indicates good thermal stability.



Figure 4.9: TGA curves of (1a- 1d)_{40 wt% APPS}

Table 4.6: Thermal properties of the poly	(imide silox	(ane)s	1a – 1	ld) _{40 wt%} APPS
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Polymers	T _d (°C)	T _d (°C)	T _d (°C)	Residual mass at
	5% Weight	5% Weight loss	50% Weight	800 °C
	loss ^[3]		loss	
1 a _{40 wt} % APPS	519	434	514	32.23
1b40 wt% APPS	531	460	547	35.71
1c _{40 wt%} APPS	514	438	565	37.49
1d _{40 wt} % APPS	486	441	558	36.28

Compared with the homopolymers [3], these poly(imide siloxane)s have lower thermal stability. This lowering of thermal stability is due to the incorporation of flexible siloxane units in the polymer backbone which degrade at a lower temperature [9]. It is worth observing in the plot that there are two humps due to the formation of copolymer. The first degradation step observed at 350 - 450 °C is due the scission of Si-C linkages which have a lower bond energy compared to C-C bond which occurs at a latter phase 500 - 600 °C where degradation of more rigid aromatic structure takes place. Hence, in general, all these polymers showed very good thermal stability in nitrogen. The residual masses observed are greater than 30% in all the polymers.

4.5.10 Mechanical properties

The mechanical properties of thin poly (imide siloxane) films are shown in Table 4.7. In general, the mechanical properties of the poly (imide siloxane) films are very good and exhibited tensile strength and modulus of measurable values. The representative stress-strain plots of $1a_{40 \text{ wt\%}}$ APPS and $1b_{40 \text{ wt\%}}$ APPS are shown in Figure 4.10. The poly (imide siloxane) containing most rigid quadriphenyl unit , $1b_{40 \text{ wt\%}}$ APPS exhibited highest tensile strength up to 30 MPa and also highest elongation at break up to 103% followed by $1a_{40 \text{ wt\%}}$ APPS which have next higher elongation at break of 73%.

Polymer	Tensile strength (MPa) ^[a]	Tensile strength (MPa)	Elongation at break ^[a] (%)	Elongation at break (%)	Young's Modulus (GPa)
la40 wt% APPS	129	28.3	22	73	0.61
1 b _{40 wt%} APPS	147	30.3	30	103	0.63
lc _{40 wt%} APPS	131	23.3	6	12	0.55
ld _{40 wt} % APPS	116	20.2	15	7	0.53

Table 4.7: Mechanical properties of $(1a - 1d)_{40 \text{ wt}\% \text{ APPS}}$

^[a] values taken from reference [3]

It is also observed that the polymers having more extended geometry $1a_{40 \text{ wt\% APPS}}$ and $1b_{40 \text{ wt\% APPS}}$ respectively results in more elongation at break than the polymers having less extended geometry. It is also worth observing that the homopolymers

Polymer	Water absorption (%)after 72 h ^[a]	Water absorption (%)after 72 h	Dielectric constant at 1 MHz ^[a]	Dielectric constant at 1 MHz
la _{40wt} % APPS	0.4	0.04	2.88	2.38
1b _{40wt%} APPS	0.4	0.02	2.82	2.36
1c _{40wt} % APPS	0.9	0.05	3.24	2.45
1d _{40wt%} APPS	0.8	0.07	3.19	2.52

Table 4.8: Water absorption and dielectric constant of (1a - 1d) 40 wt% APPS

^[a] values taken from reference [3]

4.5.12 Rheology behavior

It is interesting to know that how apparent viscosity of the polymers changes when shear rates (and stresses) are changing in a very wide range (Figure 4.12). The flow curve of the polymers showed very pronounced non-Newtonian flow with a gradual decrease of apparent viscosity. The polymers showed low melt viscosity and hence good melt processability. At low shear rates, Newtonian behavior is observed and apparent viscosity corresponding to this region of the flow curve is called zero-shear or initial or maximum Newtonian viscosity. The decrease of apparent viscosity is observed, typical of non-Newtonian behavior. The whole decrease of apparent viscosity exceeds 1000 times in comparison with the initial values.



Figure 4.12: Flow curves of (1a – 1d) 40 wt% APPS at 250 °C

4.5.13 Surface morphology

Surface morphology of the four polymers has been studied by scanning electron microscope to observe the distribution of the siloxane moiety in the polymer backbone. Figure 4.13 shows the distribution of siloxane in the polyimides under consideration indicating micro-phase separation. It is observed from the SEM micrographs that the dispersed domains are nearly spherical, domain size is relatively small and phase contrast is somewhat poor.



Figure 4.13: SEM images of (1a - 1d) 40 wt% APPS

4.6 Conclusions

Four new poly (imide siloxane)s were prepared on reaction of o-diphthalic anhydride (ODPA) with different trifluoromethyl - substituted diamines each with 40 wt% siloxane loading. The polymers were well characterized by spectroscopy, thermal, mechanical, water sorption and dielectric studies. The proton NMR indicated the siloxane loading is about 36% although it was attempted to 40 wt%. The silicone NMR confirmed that the low siloxane incorporation was due to disproportionation reaction of siloxane chain that resulted in lowering of siloxane block length. The synthesized polymers exhibited very good solubility in different organic solvents. Because of the microphase morphology of the films, the glass transition temperature of the polyimide matrix was ideally depressed only to a small extent. These poly(imide siloxane)s showed good thermal stability at 5% weight loss up to 460 °C. Transparent thin films of these poly (imide siloxane)s exhibited tensile strength up to 30 MPa and elongation at break up to 103% depending upon the structure of the repeating unit. The films of these polymers showed negligibly low water absorption of 0.02% and dielectric constant as low as 2.36 at 1 MHz.

4.7 References

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<u>CHAPTER 5A</u> NOVEL FLUORINATED POLY(ETHER IMIDE)S FROM BISPHENOL-A-DI(PHTHALIC ANHYDRIDE)

5A.1 Introduction

Multilevel interconnection technology has been essential to realize high density and high performance ultra-large scale integrated circuits (ULSIs). The interlayer dielectric film technologies are one of the most important keys for the multilevel interconnection fabrication. Polyimide (PI) films are one of the most attractive interlayer dielectric films, because of their good surface planarization characteristics, low film stress and lower relative dielectric constant than 3.5. They are also used in other high performance applications such as gas separation membranes, coatings and composite materials in aerospace industries [1-5]. The major problem of rigid polyimides is their insolubility and infusibility in their fully imidized form, leading to processing difficulties.

The conventional PI films, synthesized by aromatic compounds [6-9], have several disadvantages such as poor adhesive properties to inorganic surfaces and high leakage current at higher operating temperatures than 200 °C. To improve the adhesive properties to inorganic films, the PI films have been modified by siloxane components. Silicon-containing polyimides [10-12] have been investigated in order to improve the processability, the thermo-oxidative stability and mechanical properties by the incorporation of silicon into the polymer.

While decreasing the siloxane loading in the polymer chain from 40 wt% to 20 wt% loading using ODPA as dianhydride it led to polymer insolubility during casting film. Hence, the dianhydride system ODPA was changed and BPADA (Bisphenol-A-diphthalic anhydride) was used with the view to improve the solubility as two flexible ether linkages are present in the structure of the BPADA. Accordingly poly(imide siloxane)s with 40 wt% as well as 20 wt% siloxane loading were synthesized. Hence, this chapter reports successful synthesis of four new poly(ether imide)s and their characterization including spectroscopy, solubility, thermal, mechanical, dielectric and rheological properties while poly(ether imide)s with 40 wt% as 20 wt% siloxane loading are reported in Chapter 5B.

5A.2 Experimental

The chemicals, solvents and experimental techniques used such as elemental analysis, FTIR, ¹H-NMR, ¹³C-NMR, solubility study, GPC, DSC, DMA, TGA,

mechanical properties (tensile stress, % elongation at break, Young's modulus), water absorption and dielectric properties are already discussed in Chapter 2.

5A.3 General synthesis of poly(ether imide)s from bisphenol-A-di(phthalic anhydride)

All polymerization reactions were carried out in nitrogen atmosphere with constant flow. An equimolar amount of diamine and dianhydride monomers were used in all cases. In a 50 mL round-bottomed flask equipped with nitrogen inlet and a magnetic stirrer was charged with 0.52 g (0.908 mmol) of 4, 4'-bis (*p*-aminophenoxy- 3, 3"trifluoromethyl) terphenyl, 0.47 g (0.908 mmol) of BPADA for 2a; 0.55 g (0.85 mmol) of 4, 4'-bis (3"-trifluoromethyl-*p*-aminobiphenyl ether)biphenyl, 0.44 g (0.85 mmol) of BPADA for 2b; 0.52 g (0.907 mmol) of 2, 6-bis (3'-trifluoromethyl-*p*-aminobiphenyl ether)pyridine, 0.47 g (0.907 mmol) of BPADA for 2c; 0.53 g (0.903 mmol) of 2,5-bis (3'-trifluoromethyl-*p*-aminobiphenylether)thiopene , 0.47 g (0.903 mmol) of BPADA for 2d each with 10 mL DMF. In each case the resulting solution was stirred for 30 minutes at room temperature. The poly (amic acid) solution was cast onto clean and dry glass petridishes. The films were dried in vacuum oven at 80 °C overnight followed by 100, 150, 200, 250 °C for 1 h at each temperature and 300 °C for 30 minutes and at 350 °C for 15 minutes under nitrogen flow. Polyimide films were then removed by immersing the glass plates in boiling water. The polymerization procedure is shown in Scheme 5A.1.



Scheme 5A.1: Reaction scheme and structures of the poly(ether imide)s derived from BPADA

5A.4 Characterization

5A.4.1 Poly(ether imide) 2a



Analytical calculation for $(C_{63}H_{38}F_6O_8N_2)_n$ (1065.01)_n: Calcd. C 71.05, H 3.59, N 2.63; Found C 69.85 H 3.72 N 2.59.

IR (KBR) (cm⁻¹): 3053 (aromatic C-H stretching), 2969 (-CH₃ group in BPADA), 1778 (C=O asymmetric stretching), 1720 (C=O symmetric stretching), 1618-1507, 1444

(aromatic C=C), 1378 (C-N stretching), 1333, 1247 (C-O-C), 1136 (C-F multiple stretch bending), 745cm⁻¹(C-N bending).

¹**H-NMR (CDCl₃): δ(ppm)** 7.94 (s, 2H, H9), 7.89 (d, J =8Hz, 2H, H16,), 7.74(d, J=8Hz, 2H, H5,), 7.67 (s, 4H, H8), 7.43(m, 6H, H12 and H25), 7.34 (m, 6H, H4 and H11), 7.19 (d, J=8Hz, 4H, H20,), 7.14 (d, J=8Hz, 2H, H17,), 7.04 (d, J=8Hz, 4H, H21,), 1.76 (s, 6H, H24).

¹³C-NMR (CDCl₃): δ(ppm) 166.8, 163.9, 156.1, 154.3, 153.9, 152.7, 147.6, 138.6, 135.9, 134.2, 131.7, 128.8, 128.1, 127.5, 125.8, 125.0, 124.3, 122.1, 122.0, 121.7(q, C1, J=272 Hz), 119.9, 119.5, 111.9, 42.6(C23), 31.0(C24).

5A.4.2 Poly(ether imide) 2b



Analytical calculation for $(C_{69}H_{42}F_6O_8N_2)_n$ (1141.10)_n : Calcd.C 72.62, H 3.71, N 2.45; Found C 72.49 H 3.82 N 2.33.

IR (KBR) (cm⁻¹): 3054(aromatic C-H stretching), 2969 (-CH₃ group in BPADA), 1778 (C=O asymmetric stretching), 1724 (C=O symmetric stretching), 1600-1505, 1444 (aromatic C=C), 1376 (C-N stretching), 1331, 1247 (C-O-C), 1134 (C-F multiple stretch bending), 745 cm⁻¹(C-N bending).

¹**H-NMR (CDCl₃):** δ (**ppm**) 7.95 (s, 2H, H9), 7.90 (d, J = 8Hz, 2H, H17), 7.73(m, 6H, H5 and H10), 7.67 (d, J = 8Hz, 4H, H8), 7.43(m, 6H, H13 and H26), 7.35 (m, 6H, H12 and H4), 7.19 (d, J = 8Hz, 4H, H21), 7.14 (d, J = 8Hz, 2H, H18), 7.04 (d, J = 8Hz, 4H, H22,), 1.76 (s, 6H, H25).

¹³C-NMR (CDCl₃): δ(ppm) 166.8, 166.7, 163.9, 156.1, 153.9, 152.7, 147.6, 139.9, 138.3, 136.1, 134.2, 131.7, 128.8, 128.1, 127.6, 125.8, 125.0, 122.3, 121.7(q, C1, J=272 Hz), 120.0, 119.9, 119.6, 111.9, 42.5(C24), 31.0(C25).

5A.4.3 Poly(ether imide) 2c

$$- \underbrace{\bigcirc - 0}_{F_3C_1} \overset{4 - 5}{\longrightarrow} \overset{8}{\bigcirc} \overset{9}{\bigcirc} \overset{CF_3}{\longleftarrow} \overset{12 - 13}{\longrightarrow} \overset{0}{\longrightarrow} \overset{15 - 0}{\longrightarrow} \overset{0}{\bigcirc} \overset{20}{\bigcirc} \overset{20}{\bigcirc} \overset{21}{\bigcirc} \overset{21}{\bigcirc} \overset{0}{\bigcirc} \overset{0}{\bigcirc} \overset{21}{\bigcirc} \overset{0}{\bigcirc} \overset{0}{\bigcirc} \overset{21}{\bigcirc} \overset{0}{\bigcirc} \overset{0}{\odot} \overset{0}{ } \overset{0}{ } \overset{0}{ } \overset{0}{\odot} \overset{0}{ } \overset{0}{ }$$

Analytical calculation for $(C_{62}H_{37}F_6O_8N_3)_n$ (1065.99)_n : Calcd.C 69.85, H 3.49 N 3.94; Found C 69.77 H 3.61 N. 3.88.

IR (KBR) (cm⁻¹): 3068 (aromatic C-H stretching), 2969 (-CH₃ group in BPADA), 1777 (C=O asymmetric stretching), 1724 (C=O symmetric stretching), 1618-1500, 1444 (aromatic C=C), 1378 (C-N stretching), 1326, 1251 (C-O-C), 1133 (C-F multiple stretch bending), 744 cm⁻¹ (C-N bending).

¹**H-NMR (CDCl₃):** δ(**ppm**) 8.45 (s, 2H, H10), 8.25 (d, 2H, H17, J = 8Hz), 7.88(m, 3H, H8 and H9), 7.70 (d, J = 8Hz, 2H, H21), 7.43(m, 6H, H13 and H26), 7.34 (m, 6H, H4 and H12), 7.19 (m, 6H, H5 and H18), 7.03 (d, J = 8Hz,4H, H22,), 1.75 (s, 6H, H25).

¹³**C-NMR (CDCl₃): δ(ppm)** 166.8, 166.7, 155.7, 155.0, 152.7, 147.6, 138.1, 134.4, 134.2, 131.7, 128.8, 127.8, 125.9, 125.0, 124.4(q, C¹, J=272 Hz), 124.3, 122.2, 122.1, 119.7, 118.7, 111.9, 42.5(C24), 31.0(C25).

5A.4.4 Poly(ether imide) 2d



Analytical calculation for $(C_{61}H_{36}F_6O_8N_2S)_n$ (1071.03)_n :Calcd. C 68.40, H 3.38 N 2.61; Found C 68.35 H 3.52 N 2.55.

IR (KBR) (cm⁻¹): 3059 (aromatic C-H stretching), 2969 (-CH₃ group in BPADA), 1778 (C=O asymmetric stretching), 1724 (C=O symmetric stretching), 1600-1506, 1445 (aromatic C=C stretching), 1377 (C-N stretching), 1328, 1247 (C-O-C), 1136 (C-F multiple stretch bending), 745 cm⁻¹ (C-N bending).

¹**H-NMR (CDCl₃):** δ(**ppm**) 7.89 (d, 2H, H16, J = 10 Hz), 7.86 (s, 2H, H9), 7.69 (m, 2H, H5), 7.43(m, 6H, H12 and H17), 7.35 (m, 6H, H11 and H25), 7.29 (s, 2H, H8), 7.17 (m, 4H, H21), 7.08 (d, J = 9Hz, 2H, H4,),7.04 (d, J = 8Hz, 4H, H20,), 1.76 (s, 6H, H24).

¹³C-NMR (CDCl₃): δ(ppm) 166.8, 166.7, 163.9, 155.9, 154.2, 152.7, 147.6, 142.0, 134.2, 131.7, 130.3, 129.7, 128.8, 127.7, 125.8, 124.9.0, 124.5, 124.1, 121.7 (q, C1, J=272 Hz), 120.0, 119.6, 112.0, 42.6(C23), 31.0(C24).

5A.5 Results and discussions

5A.5.1 FTIR Spectroscopy

The formation of poly(ether imides)s was confirmed by FTIR spectroscopy. FTIR spectra the polyimide films prepared by thermal imidization method showed the absorption bands at 1780 cm⁻¹(C = O asymmetric stretching), 1720 cm⁻¹ (C = O symmetric stretching), 1378 cm⁻¹(C-N stretching), 745 cm⁻¹(C = O bending), corresponding to the characteristic imide bands. FTIR spectra of the polymers showed no absorption band at 1720 cm⁻¹ corresponding to C = O stretching of carboxylic acid and 1660 cm⁻¹ corresponding to C = O amide stretching indicating full imidization.

5A.5.2 ¹H and ¹³C –NMR spectroscopy

¹H-NMR of poly (ether imide) reveals good matching of integrated peaks for chemically different protons in all polymers. The ¹H-NMR spectre of the poly(ether imides) are presented in Figures 5A.1 - 5A-4 respectively. ¹³C-NMR spectra also support the proposed polymer structures. ¹³C-NMR spectra of the poly(ether imides) are presented in Figures 5A.5 - 5A.8 respectively.

Novel fluorinated poly(ether imide)s from bisphenol-A-di(phthalic anhydride)



Figure5A.1:¹H-NMR spectrum of poly(ether imide) 2a



Figure 5A.2:¹H-NMR spectrum of poly(ether imide) 2b



Figure 5A.4:¹H-NMR spectrum of poly(ether imide) 2d



Figure 5A.5: ¹³C-NMR spectrum of poly(ether imide) 2a



Figure 5A.6: ¹³C-NMR spectrum of poly(ether imide) 2b



Figure 5A.8: ¹³C-NMR spectrum of poly(ether imide) 2d

5A.5.3 Polymer solubility

The solubilities of the resulting poly(ether imide)s investigated in different organic solvents are presented in Table 5A.1. The polymers are observed to have good solubility in various organic solvents such as chloroform, dicholoromethane, N-methyl-2-pyrollidinone, dimethylformamide and in N, N-dimethylacetamide while insolubility is observed in case of dimethylsulfoxide as solvent. The polymers are found to be soluble in tetrahydrofuran except polymer 2b due to the presence of rigid quadriphenyl unit in the polymer backbone. Compared to the previous work [13] these polymers showed dramatic improvement in solubility due to the two ether linkages in the dianhydride moiety.

Table 5A.1: Solubilities of the poly(ether imide)s from BPADA

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	CH ₂ Cl ₂	Acetone
2a	+	+	+	-	+	+	+	_
2b	+	+	+	-	-	+	+	-
2c	+	+	+	-	+	+	+	-
2d	+	+	+	-	+	+	+	-

+, soluble at room temperature; -, insoluble at reflux

5A.5.4 Molecular weight determination of the polymers

Number average molecular weight (M_n) and polydispersity index (PDI) of the polymers were determined by gel permeation chromatography using DMAc / 2 % H₂O / (3g / l) LiCl as eluent (flow rate 0.5 ml / min) and RI detector was used to record the signal. The molecular weight of the polymers were recorded with respect to monodisperse poly(vinylpyridin). The molar masses of the poly(ether imide)s reported in Table 5A .2 indicates formation of high molar masses.

Polymers	η _{inh} (dL/g)	M _n	PDI	Film Quality
2a	0.41	32000	2.38	Clear, flexible
2b	0.43	34000	3.12	Clear, flexible
2c	0.36	28000	2.68	Clear, flexible
2d	0.35	27000	2.67	Clear, flexible

Fable5A.2: Molecular	• weight and PDI	of the poly(e	ther imide)s	from BPADA
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 $\eta_{inh} = 0.5$ weight % solution of poly(imidesiloxane)s in DMAc at 30 °C M_n = number average molecular weight PDI = polydispersity index

5A.5.5 Glass transition temperature versus polymer structure

The poly(ether imide)s exhibited no crystallization or melting transition in DSC measurements. These polymers show glass transition temperature, which indicate amorphous morphology. The glass transition values are summarized in Table 5A.3.

The polymers 2b exhibit highest T_g values than other polymers, which is due to the presence of rigid quadriphenyl unit in the backbone. The next higher glass transition temperature is observed in 2a containing rigid terphenyl unit in the polymer backbone. The following order of glass transition is obtained: quadriphenyl > 1, 4 diphenyl benzene > 2, 6-diphenyl pyridine > 2, 5 -diphenyl thiophene. This order could be explained on considering three factors: rigidity, catenation angle of different groups as shown in following scheme and the polarity as discussed in Chapter 4 (Section 4.5.7).

5A.5.6 DMA measurements

The representative dynamic mechanical behaviors of the polymer films 2a and 2b are shown in Figure 5A.10 and Figure 5A.11 respectively. The T_g 's taken from the tan ∂ peaks at 1 Hz are given in Table 5A.3. These values are in good agreement with the calorimetric T_g values. The polymers retained very good mechanical properties up to the T_g 's as observed from the storage modulus plots of the polymers.







Figure 5A.11: DMA plot of 2b

Polymer	DSC	DMA	$T_d (^{\circ} C)$	T _d (°C)	Residual mass
	$T_{g}(C)$	$(\tan \partial)$	5% Weight	5% Weight	at 800 °C in N ₂
		$T_{g}(^{\circ}C)$	loss in N ₂	loss in air	
2a	216	210	519	487	62.13
2b	228	218	522	489	63.48
2c	214	204	514	485	59.05
2d	212	202	504	470	62.29

Table 5A.3: Thermal properties of the poly(ether imide)s from BPADA

5A.5.7 Thermal stability

The thermal properties of the poly (ether imide)s were evaluated by TGA in both nitrogen and air. The TGA curves for the polymers are shown in Figure 5A.12. The thermal properties are summarized in Table 5A.3. The 5% weight loss temperature of these polymers in nitrogen is in the range of 504 - 522 °C while that in air is in the range of 470 - 489 °C. All the polymers showed very good thermal stability as expected in the case of polyimides. Lower thermal stability was observed when TGA was carried out in air compared to that in nitrogen atmosphere due to the oxidation of the thermo labile isopropylidine groups in the polymer backbone arising from BPADA.

While high residual masses are observed in case of nitrogen atmosphere, no residual masses are left when TGA is carried out in air. The lowest thermal stability of polymer 2d containing thiophene in the main chain in air is due the oxidation of thiophene to thiophene dioxide at high temperature. At high temperature thiophene loses its aromaticity and as a consequence lower thermal stability results.



Thiophene

Thiophene dioxide



(ii)

Figure 5A.12: TGA curves of the poly(ether imide)s 2a-2d in (i) $N_2\;$ (ii) air

5A.5.8 Mechanical properties

The mechanical properties of thin polyimide films cast from DMF are shown in Table 5A.4. The polymers exhibited high tensile strength up to 97 MPa and Young's modulus upto 1.56 GPa. It is observed from Table 5A.2 that the polymers having more extended geometry results in more elongation at break than the polymers having less extended geometry. Polymers 2c and 2d containing pyridine and thiophene moiety in the backbone showed less elongation at break than polymers 2a and 2b.

5A.5.9 Water absorption and dielectric behavior

Water absorption study of the poly(ether imide)s were done by immersing rectangular pieces of samples $(30 \times 10 \text{ mm})$ in double distilled water at 30 °C after taking the initial weight. Final weight was taken after 24 h and water absorption was calculated. Water absorption values of these polymers are as low as 0.19 wt% in case of polymer 2b characteristics of semifluorinated poly(ether imide)s.

The dielectric constant of the polymer films was determined from capacitance values by using capacitance meter from 100 KHz to 1 MHz at 30 °C. The water absorption and dielectric constant of the polymers are also reported in Table 5A.4.

Polymer	Tensile break (MPa)	Modulus (GPa)	Elongation at break (%)	Water Absorption (%) after 24 h	Dielectric Constant 1MHz
2a	73	1.15	10	0.24	2.79
2b	93	1.44	20	0.19	2.80
2c	97	1.43	9	0.22	3.07
2d	69	1.56	5	0.30	3.14

 Table 5A.4. Mechanical, dielectric and water absorption behavior

 of poly (ether imide)s from BPADA

5A.5.9 Rheology behavior

It is interesting to know that how apparent viscosity changes when shear rates are changing in a very wide range. The flow curve of the polymers (Figure 5A.13) showed very pronounced non-Newtonian flow with a gradual decrease of apparent viscosity. At low shear rates, Newtonian behavior is observed and apparent viscosity corresponding to this region of the flow curve is called zero-shear or initial or maximum Newtonian viscosity. Then the decrease of apparent viscosity is observed - typical of non-Newtonian behavior.



Figure 5A.13: Flow curves of the poly(ether imide)s 2a – 2d at 250 °C
5A.6 Conclusion

Four new fluorinated poly (ether imide)s were synthesized on reaction with bisphenol-A (diphthalic anhydride) with different trifluoromethyl - substituted diamines. The polymers were well characterized by spectroscopy, thermal, mechanical and dielectric properties. The synthesized polymers exhibited good solubility in different organic solvents. The resulting poly(ether imide)s were amorphous and exhibited very good thermal stability of upto 522 °C in nitrogen and 489 °C in air at 5% weight loss. These polymers showed good mechanical strength up to 97 MPa, a modulus of elasticity up to 1.56 GPa and elongation at break upto 20%. These poly(ether imide)s were observed to have low moisture uptake of 0.19 - 0.30 % and low dielectric constant of 2.79 - 3.1 at 1 MHz. and hence are promising materials for electronic applications and as gas separation membranes.

5A.7 References

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CHAPTER 5B

NOVEL FLUORINATED POLY(IMIDE SILOXANE)S DERIVED FROM BISPHENOL-A-DI(PHTHALIC) ANHYDRIDE

5B.1 Introduction

Fluorinated polyimides have attracted much attention in the electronics industry because of their properties such as low dielectric constant, low moisture absorption, low permittivity and high stability [1-4]. Incorporation of siloxane unit to polyimides and related polymers [6-8] increases the solubility and processability. Furthermore, siloxane unit impart impact resistance, biocompatibility, reduces moisture uptake and dielectric constant of the polyimides.

In this chapter we have incorporated two different levels of siloxane, 20 and 40 wt % to each of the previously reported homopolymers discussed in chapter 5A and synthesized eight new poly(imide siloxane)s. The properties of the resulting polymers have been investigated thoroughly and compared with the analogous homopolymers.

5B.2 Experimental

The chemicals, solvents and experimental techniques used such as elemental analysis, FTIR, ¹H-NMR, ¹³C-NMR, solubility study, GPC, DSC, DMA, TGA, mechanical properties (tensile stress, % elongation at break, Young's modulus), water absorption, dielectric properties and SEM are already discussed in Chapter 2.

5B.3 General synthesis of poly(imide siloxane)s from bisphenol-A-di(phthalic anhydride)

The polymerization reactions were conducted by the reaction of BPADA and two different diamines in a random fashion. In every synthesis 1 mole of BPADA and mixture of two diamines which add up to 1 mole is presented in the subscript of all the polymeric structures respectively. The reactions were conducted under constant flow of nitrogen. A representative polymerization procedure with 40 wt% loading of APPS is as follows.

The polymers were prepared by conventional one pot solution imidization method. Orthodichorobenzene, ODCB was used with a solid content of 20 wt%.

In a 50 mL, 3 necked round - bottomed flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with 0.82 g (1.57 mmol) BPADA, 0.375 g (0.64 mmol) of 4,4'-bis(*p*-aminophenoxy- 3,3''-trifluoromethyl) terphenyl and APPS 0.804 g (0.93 mmol) and 20 mL of 1,2-

dichorobenzene. The temperature was raised slowly from room temperature to 180 °C. During the course of reaction, water formed due to imidization was removed azeotropically by ODCB and accordingly the fresh solvent was added to makeup for the solvent loss. During the reaction, the solution was observed to turn viscous. The reaction was continued for 6 h at 180 °C under nitrogen. The resulting viscous polymeric solution was then cooled to room temperature and was precipitated in 500 mL methanol.



Scheme 5B.1: Reaction scheme and chemical structures of (2a -2d) with 40 wt % and 20 wt% siloxane loading

The fibrous product obtained was dried and dissolved in 20 mL dichloromethane and re-precipitated from methanol. The products were dried at 120 °C for 5 h under vacuum and were used for further analysis. The reaction scheme and polymer structures are shown in Scheme 5B.1. A weighed quantity of polymers was dissolved in a measured amount of dichloromethane (15 wt%) and was poured in flat bottom Petri dishes to obtain polymer films. The Petri dishes were covered and the solvent was allowed to evaporate at a controlled rate at 30 °C over night. The Petri dishes were then kept in a vacuum oven and the temperature of the oven was slowly raised to 120 °C and kept under continuous vacuum for 5-6 h to remove any trace of solvent.

5B.4 Characterization

5B.4.1 Poly (imide siloxane) - 2a40wt% APPS



Analytical calculation for $(C_{58,29115} H_{70.9574} F_{2.46} O_{12.3129} N_2 Si_{6.0829}n (1232.72 gmol⁻¹)_n : C, 58.29; H, 5.80; N, 2.27 Found : 60.0; H, 5.75; N, 2.49.$

IR (KBR) (cm⁻¹): 3068 (aromatic C-H stretching), 2962 (-CH₃ group present in APPS); 1773 and 1716 (asymmetric and symmetric –CO- stretching); 1601 (C=C ring stretching); 1506, (band due to C-F stretching); 1392 (asymmetric C-O-C stretching); 1084, 1021 (Si-O-Si stretching); 800 (Si-C stretching).

¹**H-NMR (CDCl₃):** δ (**ppm**) 7.96 - 7.01(21.23 H), 3.64(s, 2.05H, -CH₂-N<), 1.75(s, 8.36H,-CH₂-), 0.91 - 0.51(s, 2.05H, -CH₂-Si), 0.28 - 0.01(m, 32.36H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.9, 166.8, 163.3, 156.0, 154.3, 152.8,147.42, 138.6, 135.9, 134.7, 134.2, 131.7, 131.2, 128.6, 128.1, 127.5, 125.8, 125.0, 123.0, 122.3, 120.4, 119.9, 119.6, 112.0, 111.6, 42.5, 40.9,31.0,22.6, 15.3.

5B.4.2 Poly (imide siloxane) - 2b40wt% APPS



Analytical calculation for $(C_{62.1151} H_{73.3753} F_{2.37} O_{12.4225} N_2 Si_{6.2375})_n (1267.04 \text{ gmol}^{-1})_n : C, 58.88; H, 5.83; N, 2.21 Found : C, 59.22; H, 5.76; N, 2.59.$

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2962(-CH₃ group present in APPS); 1773 and 1716 (asymmetric and symmetric –CO- stretching); 1602 (C=C ring stretching); 1504, (band due to C-F stretching); 1389 (asymmetric C-O-C stretching); 1083, 1020 (Si-O-Si stretching); 800 (Si-C stretching).

¹**H-NMR (CDCl₃):** δ (**ppm**) 7.97 – 7.01(20.99H), 3.64(s, 2.2H, -CH₂-N<), 1.76(s, 8.42H, -CH₂-), 0.91 – 0.54(s, 2.2H, -CH₂-Si), 0.28 – 0.01(m, 29.62H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.9, 166.8, 163.9, 163.3, 156.1, 154.2, 152.9, 147.4, 139.9, 138.3, 136.1, 134.7, 134.2, 131.6, 128.6, 128.1, 125.8, 125.0, 123.0, 122.3, 120.4, 119.9, 119.6, 112.0, 111.6, 42.5, 40.9, 31.0, 22.6, 15.3.

5B.4.3 Poly (imide siloxane) – 2c_{40wt% APPS}



Analytical calculation for $(C_{59,4158} \text{ H}_{70.5474} \text{ F}_{2.46} \text{O}_{12.4225} \text{ N}_{2.41} \text{ Si}_{6.0829})_n (1234.88 \text{ gmol}^{-1})_n : C, 57.79; H, 5.75; N, 2.73 \text{ Found} : C, 58.23; H, 5.69; N, 3.10$

IR (KBR) (cm⁻¹): 3064(aromatic C-H stretching); 2962(-CH₃ group present in APPS); 1773 and 1717 (asymmetric and symmetric –CO- stretching); 1600 (C=C ring stretching); 1502, (band due to C-F stretching); 1382 (asymmetric C-O-C stretching); 1085, 1022 (Si-O-Si stretching); 801 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 8.48 - 7.00(18.42 H), 3.64(s, 1.50H, -CH₂-N<), 1.75(s, 8.36H,-CH₂-), 0.91 - 0.54(s, 1.93H, -CH₂-Si), 0.28 - 0.01(m, 28.52H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.9, 166.7, 163.9, 163.3, 155.8, 155.4, 155.6, 155.1, 152.9, 147.6, 147.4, 138.1, 134.7, 134.2, 131.7, 128.6, 128.1, 127.7, 126.0, 125.8, 125.0,123.0, 122.3, 119.9, 118.7, 112.0, 111.6, 42.5, 40.9,31.0,22.6, 15.3.





Analytical calculation for $(C_{59} H_{70.1374} F_{2.46} O_{12.3129} N_2 Si_{6.0829} S_{0.41})_n (1235.19 \text{ gmol}^{-1})_n : C, 57.37; H, 5.72; N, 2.26 Found : 58.21; H, 5.32; N, 2.55.$

IR (KBR) (cm⁻¹): 3068 (aromatic C-H stretching), 2962(-CH₃ group present in APPS); 1774 and 1717 (asymmetric and symmetric –CO- stretching); 1601 (C=C ring stretching); 1504, (band due to C-F stretching); 1389 (asymmetric C-O-C stretching); 1085, 1022 (Si-O-Si stretching); 801 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 7.93 – 7.01(20.52H), 3.64(s, 1.86H, -CH₂-N<), 1.76(s, 8.36H,-CH₂-), 0.91 – 0.54(s, 1.86H, -CH₂-Si), 0.28 – 0.01(m, 34.73H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.9, 166.7, 163.9, 163.3, 155.9, 154.2, 147.6, 142.0, 134.7,134.2, 130.3, 129.6, 128.6, 128.1, 127.7, 125.8, 125.0, 124.5, 123.1, 122.3, 120.4, 119.9, 119.6, 112.0, 111.6, 42.5, 40.9,31.0,22.6, 15.3.

5B.4.5 Poly (imide siloxane) - 2a_{20wt%} APPS



Analytical calculation for $(C_{61.5312} H_{53.2497} F_{4.362} O_{9.9956} N_2 Si_{2.8146})_n (1142.61 \text{ gmol}^{-1})_n : C, 64.68; H, 4.69; N, 2.45 Found : C, 64.93; H, 4.21; N, 2.63.$

IR (KBR) (cm⁻¹): 3062 (aromatic C-H stretching), 2963(-CH₃ group present in APPS); 1777 and 1722 (asymmetric and symmetric –CO- stretching); 1618 (C=C ring stretching); 1506, (band due to C-F stretching); 1377 (asymmetric C-O-C stretching); 1080, 1015 (Si-O-Si stretching); 800 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 7.94 – 7.03(28.56H), 3.61(s, 1.55H, -CH₂-N<), 1.74(s, 7.092H,-CH₂-), 0.91 – 0.55(s, 1.86H, -CH₂-Si), 0.28 – 0.01(m, 13.20H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.9, 163.9, 156.0, 154.3, 152.7, 147.6, 138.6, 135.9,134.2, 132.6, 131.7, 130.5, 129.8, 128.8, 128.1, 127.5, 125.8, 125.0, 123.1, 122.3, 120.4, 120.0, 119.6, 111.9, 111.6, 42.6, 40.9,31.0,22.6, 15.3.

5B.4.6 Poly (imide siloxane) – 2b_{20wt%} APPS



Analytical calculation for Anal calc. for $(C_{65.7396} H_{56.8578} F_{4.281} O_{10.0943} N_2 Si_{2.9538})_n$ (1200.74 gmol⁻¹)_n : C, 65.76; H, 4.77; N, 2.33 Found : C, 65.40; H, 4.63; N, 2.46

IR (KBR) (cm⁻¹): 3061 (aromatic C-H stretching), 2961(-CH₃ group present in APPS); 1777 and 1723 (asymmetric and symmetric –CO- stretching); 1600 (C=C ring stretching); 1503, (band due to C-F stretching); 1376 (asymmetric C-O-C stretching); 1079, 1015 (Si-O-Si stretching); 799 (Si-C stretching).

¹**H-NMR (CDCl₃):** δ (**ppm**) 7.95 - 7.04(34.28 H), 3.63(s, 1.11H, -CH₂-N<), 1.76(s, 7.146H, -CH₂-), 0.91 - 0.55(s, 1.11H, -CH₂-Si), 0.28 - 0.01(m, 19.18H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.8, 166.6, 163.8, 156.0, 154.0, 152.6, 147.5, 139.7, 138.1, 136.0, 134.1, 131.5, 128.6, 128.5, 128.0, 127.5, 127.3, 125.6, 124.9, 123.0, 120.2, 119.8, 119.4, 111.8, 111.4, 42.4, 40.8, 31.0, 22.5, 15.2.

5B.4.7 Poly (imide siloxane) – 2c_{20wt% APPS}



Analytical calculation for $(C_{60.8042} \text{ H}_{52.5227} \text{ F}_{4.362} \text{ O}_{9.9956} \text{ N}_{2.727} \text{ Si}_{2.8146})_n (1143.33 \text{ gmol}^{-1})_n$: C, 63.87; H, 4.63; N, 3.34 Found : C, 63.55; H, 4.29; N, 3.33.

IR (KBR) (cm⁻¹): 3066 (aromatic C-H stretching), 2963(-CH₃ group present in APPS); 1777 and 1723(asymmetric and symmetric –CO- stretching); 1610 (C=C ring stretching); 1500, (band due to C-F stretching); 1378 (asymmetric C-O-C stretching); 1080, 1016 (Si-O-Si stretching); 802 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 8.45 - 7.03(27.34 H), 3.63(s, 1.40H, -CH₂-N<), 1.76(s, 7.092H,-CH₂-), 0.91 - 0.55(s, 1.40H, -CH₂-Si), 0.28 - 0.01(m, 13.61H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.9, 166.7, 163.9, 155.8, 155.6,156.0, 152.7, 152.9, 147.6, 138.1,134.4, 134.2, 131.7, 130.5, 128.7, 128.1, 127.2, 126.0, 125.8,125.0, 123.1, 122.4, 120.0, 119.7, 118.7, 111.9, 42.6, 40.9, 31.0, 22.6, 15.3.

5B.4.8 Poly (imide siloxane) - 2d_{20wt% APPS}



Analytical calculation for $(C_{60.0738} H_{51.8536} F_{4.356} O_{10.0029} N_2 Si_{2.8249} S_{0.726})_n$ (1147.27 gmol⁻¹)_n : C, 62.89; H, 4.55; N, 2.44 Found : C, 63.22; H, 4.29; N, 2.55.

IR (KBR) (cm⁻¹): 3068(aromatic C-H stretching); 2964(-CH₃ group present in APPS); 1776 and 1722 (asymmetric and symmetric –CO- stretching); 1602 (C=C ring stretching); 1506, (band due to C-F stretching); 1377 (asymmetric C-O-C stretching); 1082, 1019 (Si-O-Si stretching); 801 (Si-C stretching).

¹**H-NMR (CDCl₃):** δ (**ppm**) 7.91 – 7.03(24.95 H), 3.63(s, 1.46H, -CH₂-N<), 1.76(s, 7.096H, -CH₂-), 0.91 – 0.57(s, 1.76H, -CH₂-Si), 0.28 – 0.01(m, 11.85H, Si-CH₃).

¹³C-NMR (CDCl₃): δ(ppm) 167.9, 166.8, 163.9, 163.3, 156.0, 154.3, 152.9, 152.7, 147.4, 138.6, 135.9, 134.7, 134.2, 131.7, 128.6, 128.1, 127.6, 125.8, 125.0, 123.0, 122.3, 122.3, 120.4, 119.9, 119.6, 112.0, 111.6, 42.5, 40.9, 31.0, 22.6, 15.3.

5B.5 Results and discussions

5B.5.1 FTIR spectroscopy

The formation of poly (imide siloxane) was confirmed by FTIR spectroscopy. FTIR spectra of the polyimide films showed the absorption bands at about 1780 cm⁻¹ (C=O asymmetric stretching), 1730 cm⁻¹ (C=O symmetric stretching), corresponding to imide bands. Strong absorption band at 2960 cm⁻¹ was due to the presence of methyl groups attached to silicon molecules in APPS and from BPADA. No detectable absorption band was observed at 3400-3100 cm⁻¹ corresponding to amide (-NH-) and acid (-OH) stretching and 1660 cm⁻¹ corresponding to amide stretching of C=O bond indicating complete imidization. Strong absorption bands at 1090, 1020 cm⁻¹ (Si-O-Si stretching) and 800 cm⁻¹ (Si-C) were the characteristic peaks due to the presence of siloxane units in the polymer backbone.

5B.5.2 ¹H - NMR spectroscopy

¹H-NMR spectra of the polymers also did not show any amide or acid protons, indicating full imidization. There was very good matching of integrated peak areas for different chemically different protons present in all the eight polymers.

The siloxane incorporation in the polymers was calculated from the integrated peak areas of the proton NMR spectra. Table 5B.1 represents the number of aromatic and aliphatic protons calculated from the structures of poly (imide siloxane)s and their ratio and that found from integrated peak areas of the proton NMR spectra. In each of the respective cases it is observed that the ratio of aromatic/aliphatic protons found from the integrated peak areas is more than that calculated values from gross molecular structure. It is observed that the poly(imide siloxane)s have been prepared with the view of incorporating 40 wt% siloxane loading the actual incorporation found is around 36-38 wt % while 17-18 wt % incorporation has been observed when we tried to incorporate 20 wt % of siloxane in the polymer backbone. The reasons for less siloxane incorporation have been discussed in detail in Chapter 4 (Section 4.5.4).

Polymer	C-aro	C-ali	F-aro	F-ali	C-ali/aro	F-ali/aro	A - Silo %
2a40wt% APPS	21.38	49.57	21.23	44.82	2.318	2.111	36.41
2b _{40wt%} APPS	22.69	50.68	20.99	42.43	2.233	2.020	36.18
2c _{40wt%} APPS	20.97	49.57	18.42	40.31	2.363	2.188	37.03
$2d_{40wt\%}$ APPS	20.56	49.57	20.52	46.81	2.410	2.280	37.83
2a20wt% APPS	27.08	26.16	28.56	23.70	0.96	0.83	17.17
2b _{20wt%} APPS	29.69	27.16	34.28	28.56	0.91	0.84	18.21
2c _{20wt%} APPS	26.35	26.16	27.34	23.51	0.99	0.86	17.32
2d _{20wt%} APPS	25.61	26.23	24.95	22.17	1.024	0.89	17.34

Table 5B.1: Actual incorporation of siloxane in (2a – 2d) with 40 wt% APPS and 20 wt% APPS from ¹H-NMR spectra

C-aro = Theoretical number of aromatic protons calculated from structure

C-ali = Theoretical number of aliphatic protons calculated from structure

C (ali/aro) = Theoretical ratio of aromatic/aliphatic protons

F(ali/aro) = Found ratio of aromatic/aliphatic protons calculated from integrated peaks A-silo (%) = [F(ali/aro)/C(ali/aro)x 40] = Actual wt% incorporation of siloxane in the polymer structure.

5B.5.3 ¹³C – NMR spectroscopy

The proton decoupled ¹³C-NMR spectra support the formation of the polymers. The ¹³C-NMR signals matches with the expected number of magnetically different carbons.

5B.5.4 Polymer solubility

The solubilities of the resulting poly (imide siloxane)s were investigated in different organic solvents. Solubility behavior of the polymers in different solvents is presented in Table 5B.2. These polymers exhibited very good solubility in common organic solvents such as and NMP, DMF, DMAc, THF, chloroform, dichloromethane and was observed to be insoluble in DMSO and acetone. In comparison to the analogous homopolymers in Chapter 5A, these polymers exhibited dramatic improvement in solubility. As expected this is due to the siloxane units incorporated into the polyimide backbone that increased the chain flexibility contributing the ease of the polymer to solvent attack. The polymers showed excellent solubility behavior with 20 wt% siloxane loading when BPADA is used as dianhydride. This enhanced solubility in this series of polymers is attributed to the highly flexible nature of BPADA in comparison to the solubility of ODPA having only one ether linkage. Indeed the siloxane loading has a significant role in polymer solubility; an optimization of siloxane loading for a specified application of these materials is required.

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	CH ₂ Cl ₂	Acetone
2a40wt% APPS	+	+	+	-	+	+	+	-
2b _{40wt%} APPS	+	+	+	-	+	+	+	-
$2c_{40wt\%}$ APPS	+	+	+	-	+	+	+	-
2d40wt% APPS	+	+	+	-	+	+	+	-
2a _{20wt%} APPS	+	+	+	-	+	+	+	-
2b _{20wt%} APPS	+	+	+	-	+	+	+	-
2c _{20wt%} APPS	+	+	+	-	+	+	+	-
2d _{20wt%} APPS	+	+	+	-	+	+	+	-

Table 5B.2: Solubilities of (2a -2d) with 40 wt% and 20 wt% siloxane loading

+, soluble at room temperature; -, insoluble at reflux

5B.5.5 Molecular weight determination of the poly(imide siloxane)s

Number average molecular weight (M_n) and polydispersity index (PDI) was determined by gel permeation chromatography. The molar masses of the poly (imide siloxane) reported in Table 5B.3 indicate formation of high molar masses.

Polymer	η _{inh} dL/g	M _n (g/mol)	PDI
2a40wt% APPS	0.395	32,400	2.14
2b _{40wt% APPS}	0.339	42,000	2.23
2c _{40wt%} APPS	0.294	21,300	1.95
2d _{40wt%} APPS	0.298	32,200	2.34
2a _{20wt% APPS}	0.435	35,500	1.93
2b _{20wt% APPS}	0.541	55,900	2.41
2c _{20wt} % APPS	0.375	25,600	1.73
2d _{20wt%} APPS	0.428	48,700	2.16

Table 5B.3: Molecular weight and PDI of (2a -2d) with 40 wt % and 20 wt% siloxane loading

 η_{inh} , 0.5 weight % solution of poly(imidesiloxane)s in DMAc at 30 °C M_n = number average molecular weight PDI = Polydianarity index

PDI = Polydispersity index

5B.5.6 Glass transition temperature versus polymer structure

The poly (imide siloxane)s exhibited no crystallization or melting transition in DSC measurements. These polymers show glass transition temperature, which indicates amorphous or glassy morphology. DSC curves of the polymers are shown in Figure 5B.1 and 5B.2 indicating glass transition temperatures of poly(imide siloxane)s with 40 wt% and 20 wt% siloxane loading respectively. The glass transition values of the synthesized poly(imide siloxane)s are summarized in Table 5B.4. In comparison to the poly(imide siloxane)s synthesized from ODPA discussed in Chapter 4, these poly(imide siloxane)s showed a marked decrease in the T_g values probably due to two ether linkages present in the BPADA. Hence, greater flexibility led to lower glass transition temperatures. Compared to the homo poly(ether imide)s synthesized from BPADA discussed in

Chapter 5A these poly(imide siloxane)s showed lower glass transition temperature and as expected the glass transition temperatures decreased as the siloxane loading was increased.

Polymer	DSC T _g (°C)	DMA (tan ∂) T _g (°C)
2a40wt% APPS	74	106
2b40wt% APPS	107	114
$2c_{40wt\%}$ APPS	69	110
2d _{40wt%} APPS	85	107
$2a_{20wt\%}$ APPS	132	146
2b _{20wt} % APPS	143	161
$2c_{20wt\%}$ APPS	125	150
2d _{20wt%} APPS	144	151

Table 5B.4: Glass transition temperatures of (2a -2d) with40 wt% and 20 wt% siloxane loading



Figure 5B.1: DSC plots of (2a-2d) 40 wt % APPS



Figure 5B.2: DSC plots of (2a-2d) 20 wt % APPS

5B.5.7 DMA measurements

The storage modulus values and T_g's taken from the tan ∂ peaks at 1Hz are given in Table 5B.5. The tan ∂ values show a maximum at a particular temperature, which in turn indicates the T_g's of the polymers. These values are not in very good agreement with the DSC T_g values in comparision to the analogous homopolymers. In fact, a higher loading of siloxane showed a gross anomaly in DSC and DMA T_g's, though the polymers with 20 wt% siloxane loading showed good agreement in DSC and DMA T_g's. DMA plots of the polymers (2a -2d)_{40wt % APPS} and (2a - 2d)_{20wt% APPS} are shown in Figure 5B.3 and Figure 5B.4 respectively. The polymers $2a_{20wt% APPS} - 2d_{20wt% APPS}$ show higher storage modulus values than the polymers $2a_{40wt% APPS} - 2d_{40wt % APPS}$ which is obvious because flexibility gets reduced by less siloxane incorporation.

with 40 wt	with 40 wt % and 20 wt% siloxane loading					
Polymer	Storage Modulus (MPa) at 40 °C	DMA (tan ∂) T _g (°C)				
2a40wt% APPS	772	106				
2b _{40wt% APPS}	918	114				
2c _{40wt%} APPS	748	110				
2d _{40wt%} APPS	810	107				
2a20wt% APPS	1666	146				
2b _{20wt%} APPS	1723	161				
$2c_{20wt\%}$ APPS	1595	150				
2d _{20wt% APPS}	1522	151				

Table 5B.5: Storage modulus and Tan ∂ values of (2a -2d) with 40 wt % and 20 wt% siloxane loading



Figure 5B.3: DMA plots of (2a - 2d)40wt% APPS



Figure 5B.4: DMA plots of $(2a - 2d)_{20wt\% APPS}$

5B.5.8 Thermal stability

The thermal properties of the copolymers were evaluated by TGA. The TGA thermograms of the polymers with 40 wt% and 20 wt% under nitrogen are presented in Figure 5B.5 and Figure 5B.6 and the thermal properties of the polymers are summarized in Table 5B.6. In general, the polymers showed good thermal stability, the 5% weight

loss temperature of the polymers are governed by the siloxane loading. Higher the siloxane loading lower is the decomposition temperature. The copolymers showed lower thermal stability than their corresponding homopolymers. The low thermal stability of these polymers is due to the presence of weak aminopropyl silane linkers in the polymer chain. Futhermore, thermal degradation begins at the Si-C bonds of PDMS because the bond dissociation energy is lower than that of the other bonds [9]. Compared to the rest, the polymers $2b_{40wt\%}$ APPs and $2b_{20wt\%}$ APPs have been observed to show greater thermal stability in nitrogen due to the presence of rigid quadriphenyl unit in the polymer structure.

Polymer	T _d (°C)	Char residue At 800 °C in N ₂
$2a_{40wt\%}$ APPS	448	26.95
2b _{40wt} % APPS	453.2	30.11
$2c_{40wt\%}$ APPS	447.7	30.20
2d _{40wt%} APPS	448.1	28.91
$2a_{20wt\%}$ APPS	452.3	45.10
2b _{20wt%} APPS	459	44.67
2c _{20wt%} APPS	453.5	45.22
2d _{20wt%} APPS	458.1	46.10

Table5B.6: Thermal Properties of the (2a -2d) with 40 wt% and 20 wt% siloxane loading

 $T_d = 5\%$ Weight loss in N_2



Figure 5B.5: TGA plots of (2a-2d) 40 wt% APPS in N2



Figure 5B.6: TGA plots of (2a-2d) 20 wt% APPS in N2

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Thermogravimetric analyses of the poly(imide siloxane)s were also studied in synthetic air. The TGA thermograms of the polymers are shown in Figure 5B.7 and Figure 5B.8 and the thermal properties of the polymers are summarized in Table 5B.7. The copolymers undergo two step degradation. The first step decomposition occurs between 380 – 450 °C for the polymers containing 40 wt% siloxane loading and between 410 – 480 °C for the polymers containing 20 wt% siloxane loading. The second step decomposition occurs between 500 - 600 °C for the polymers containing 40 wt% siloxane loading and between 550 - 615 °C for the polymers containing 20 wt% siloxane loading where at the end a white residue is left at about 600 °C. Increasing amount of siloxane in the copolymer leads to progressively less thermo-oxidatively stable polymer, but to a higher amount of residue. The first degradation step is probably due to scission of aliphatic linkages in the polymer backbone which is the polydimethylsiloxane unit incorporated in the polymer structure. The aromatic structure undergoes degradation at higher temperature. The char residue calculated from the gross polymer structure accounting the exact siloxane incorporation from ¹H-NMR spectra was correlated with the char residue obtained from TGA analysis. At a temperature ~ 600 °C the calculated char residues are in good agreement with that char residues obtained from TGA analyses which consist of silica as the main constitutent as APPS on degradation leads to the formation of white crystalline solid silica.

Incorporation of flexible linkage in varying the siloxane loading allows manipulation of properties such as thermal and thermo-oxidative stability. This degradation pattern makes the siloxane-containing polyimides potential candidates for use as ablation materials. This ability of some polymers to briefly withstand extremely high temperatures is important for their application in, for example, missile nose cones. Whereas ceramics melt and metals vaporize, these polymers carbonize, thus maintaining a protective thermal barrier. Siloxane-containing polymers which leave a residue of SiO₂ bound in a carbonized matrix could afford even more efficient protection.



Figure 5B.7: TGA plots of (2a-2d) 40 wt% APPS in air



Figure 5B.8: TGA plots of (2a-2d) 20 wt % APPS in air

Polymer	T _d (°C)	FW g mol ⁻¹	SiO ₂ % Theo	A-Silo %	SiO ₂ % _{Cald}	SiO ₂ % _{TGA-} Air
2a _{40 wt} % APPS	420	1232.72	29.60	36.41	26.95	27.90
2b _{40 wt} % APPS	422	1267.04	29.53	36.18	26.72	27.64
$2c_{40}$ wt % APPS	409	1234.88	29.55	37.03	27.36	27.26
$2d_{40}$ wt % APPS	403	1235.19	29.54	37.83	27.94	28.84
$2a_{20 wt \% APPS}$	423	1142.61	14.77	17.17	12.69	12.59
2b _{20 wt} % APPS	425	1200.74	14.31	18.21	13.04	12.80
$2c_{20 wt}$ % APPS	422	1143.33	14.77	17.32	12.79	12.72
$2d_{20 \text{ wt \% APPS}}$	421	1147.27	14.82	17.34	12.85	12.79

Table5B.7: Thermal properties of (2a -2d) with 40 wt % and 20 wt% siloxane loading in air

 $T_d = 5\%$ Weight loss in air

FW = repeat unit weight

 $SiO_2 \%_{Theo} = [(Molecular weight of SiO_2 x Total no. of elemental silicon from FW)/FW] x 100$

A-Silo % = Actual wt% incorporation of siloxane in the polymer structure

 $SiO_2 %_{Cald} = Char residue accounting exact siloxane incorporation from NMR analysis =$ $[SiO_2 % Theo x A-silo (%)] / Siloxane wt % attempted$

 $SiO_2 \%_{TGA-AIR}$ = Char residue left at 600° C from TGA analyses under air atmosphere

5B.5.9 Mechanical properties

The mechanical properties of thin poly(imide siloxane) films are shown in Table 5B.7. In general, the mechanical properties of the poly (imide siloxane) films are very good. Compared to the previously reported poly(imide siloxane)s discussed in Chapter 4, these poly(imide siloxane)s with 40 wt% siloxane incorporation show very high elongation at break. This may be due to the combined effect of the flexible siloxane units and well as the flexibility imparted by the BPADA structure containing two ether linkages.

Polymer	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
2a40wt% APPS	18.60	90	750
2b _{40wt} % APPS	24.27	144	890
2c _{40wt} % APPS	22.21	63	730
2d _{40wt} % APPS	19.82	90	833
$2a_{20wt\%}$ APPS	51.00	30	1010
2b _{20wt%} APPS	57.00	37	1230
$2c_{20wt\%}$ APPS	44.00	25	1260
2d _{20wt%} APPS	48.40	18	1300

Table 5B.7: Mechanical behavior of (2a -2d) with40 wt % and 20 wt% siloxane loading

The poly(imide siloxane), 2b containing most rigid quadriphenyl unit with 40 wt% APPS loading exhibited highest tensile strength up to 24 MPa and also high elongation at break up to 144% while the polymer 2b with the same rigid unit but with lesser incorporation of 20 wt% siloxane loading showed more tensile strength upto 57 MPa and lesser elongation at break of 37%. Figure 5B.9 shows the Stress - strain plots of the polymers (2a -2d) containing 40 wt% siloxane loading. Tensile strength values of these synthesized poly(imide siloxane)s were however lower when compared with the respective homopolymers discussed in Chapter 5A, due to the incorporation of flexible aminopropyl linkages. It is also quite interesting to note the elongation at break of the polymers with variation in siloxane loading. Decreasing the siloxane loading to 20 wt% have reduced the elongation at break to a considerable extent but higher than that of the homopolymers synthesized from BPADA. Such variation is due to the extent of flexibility imparted which comes from the plasticization effect of polydimethylsiloxane. It will be quite interesting to investigate the impact properties of these polymers as it is expected that the siloxane loading will affect great extent to the impact strength of these polymers.



Figure 5B.9: Stress – strain plot of the (2a -2d) with 40 wt% APPS

5B.5.10 Water absorption study and dielectric behavior

Water absorption study is an important parameter for materials to be used in electronic applications. Water absorption study of the poly(imide siloxane) were done by immersing rectangular pieces of samples (30x10 mm) in double distilled water at 30 °C after taking the initial weight. Final weight was taken after 24 h and % water absorption was calculated. Table 5B.8 shows the water uptake values as low as 0.02 % in case of the polymer $2b_{40}$ wt% APPS and as 0.11% for polymer $2b_{20}$ wt% APPS and these values are appreciably lower compared to the corresponding homopolymers. Negligible small water uptake of these polymers is possibly due to the contribution both from fluorine and siloxane sequences into the backbone of the polyimide backbone. The dielectric constant is also observed to decrease with incorporation of siloxane loading in the polymer backbone. The decrease in dielectric constant values as shown in Table 5B.8 is also in accordance with the increase in siloxane loading from 20 wt% to 40 wt%. This is probably due to the combined effect of fluorine as well as siloxane units present in the polymer backbone.

Polymer	Water absorption (%) after 24 h	Dielectric constant At 1 MHz
2a40wt% APPS	0.03	2.39
2b _{40wt} % APPS	0.02	2.43
2c _{40wt%} APPS	0.06	2.56
2d _{40wt} % APPS	0.08	2.59
2a _{20wt% APPS}	0.15	2.71
2b _{20wt%} APPS	0.11	2.63
2c _{20wt%} APPS	0.17	2.93
2d _{20wt%} APPS	0.20	3.06

Table 5B.8: Water absorption and Dielectric behavior of (2a -2d)with 40 wt% and 20 wt% siloxane loading

5B.5.11 Rheology behavior

It is interesting to know that how apparent viscosity changes when shear rates (and stresses) are changing in a very wide range. The flow curve of the polymers in Figure 5B.10 showed very pronounced non-Newtonian flow as a gradual decrease of apparent viscosity. With decrease in siloxane loading higher viscosity is observed at a constant temperature of 190 °C. The polymers showed low melt viscosity and hence good melt processability. At low shear rates, Newtonian behavior is observed and apparent viscosity corresponding to this region of the flow curve is called zero-shear or initial or maximum Newtonian viscosity. Then the decrease of apparent viscosity is observed - typical of non-Newtonian behavior.



Figure 5B.10: Flow curves of (2a -2d) (i) 40 wt% loading (ii) 20 wt% loading at 190 °C

5B.5.12 Surface morphology

Surface morphology of the polymers has been studied by scanning electron microscope to observe the distribution of the siloxane moiety in the polymer backbone. Figure 5B.11 shows the distribution of siloxane in the polyimidesiloxane) 2a with 40 wt % and 20 wt% siloxane loading indicating micro-phase separation. It is observed from

the SEM micrographs that the dispersed domains are nearly spherical, domain size is relatively small and phase contrast is somewhat poor. By viewing the SEM micrographs, dense incorporation of siloxane is observed in polymer 2a40wt % APPS compared to 2a20wt % APPS due to greater siloxane loading therein. Figure 5B.12 shows the representative AFM image of polymer 2b40 wt % APPS showing 2- dimensional and 3-dimensional view. AFM image shows surface roughness of about 120 nm.



(ii)

Figure5B.11: SEM micrographs of the polymers (i)2a40wt % APPS (ii)2a20wt % APPS



Figure 5B.12: AFM image of 2b40wt % APPS

5B.6 Conclusion

Eight new poly (imide siloxane)s were prepared on reaction of bisphenol-Adi(phthalic anhydride) with four different trifluoromethyl- substituted diamines with two different level of siloxane loading (40% and 20%). The polymers were well characterized by spectroscopy, thermal, mechanical, water sorption, dielectric and rheology studies. The proton NMR indicates the siloxane incorporation is 5 - 10% lower than the attempted values. The synthesized polymers exhibited very good solubility in different organic solvents. The resulting poly(imide siloxane)s were amorphous with reasonably good thermal stability. The polymers showed low tensile strength but high elongation at break with increase in siloxane loading. The polymer films absorbed negligibly small amount of water of 0.02% and 0.11% for the polymers having 40 and 20 wt% siloxane respectively. The polymers showed low dielectric constant depending on the incorporation of siloxane. These polymers may find application in high temperature cable.

5B.7 References

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5C.1 Introduction

It is well known that incorporation of siloxane unit to polyimides and related polymers [1-2] makes it possible to increase the solubility and processability and furthermore to impart impact resistance, biocompatibility, low moisture uptake, low dielectric constant, thermooxidative resistance, low surface energy and good adhesion to substrate. Silicone rubbers are the most widely used polymers in medical applications because of the strong Si-O-Si (siloxane) backbone, which provides enhanced chemical inertness and exceptional flexibility [3]. Presence of siloxane units also lead to hydrophobic surface which leads to dramatic reduction in the amount of water uptake and dielectric constant by the copolymer compared with the unmodified homopolymer analogue [4].

Further interest of how thermal, mechanical and dielectric properties of the poly(imide siloxane)s vary with variation in siloxane loading, eight new poly(imide siloxane)s have been synthesized from the same dianhydride namely BPADA and with the same fluorinated diamine namely 4, 4'-bis(3"-trifluoromethyl-p-aminobiphenyl ether) biphenyl [5] but with varying weight percentage of amino-propyl terminated polydimethylsiloxane (APPS). The polymers were synthesized by varying the siloxane loading to 5, 10, 15, 25, 30, and 35% respectively. The polymers $2b_{40}$ wt% APPs and $2b_{20}$ wt% APPs containing 40 and 20 wt% siloxane loading are already reported in Chapter 5B (Section 5B.4.2 and 5B.4.6) and are hence not reported in this chapter. The properties of all the poly(imide siloxane)s with 5, 10, 15, 20, 25, 30, 35 and 40 wt% siloxane loading were then compared with the non-siloxane analogue 2b discussed in Chapter 5A.

5C.2 Experimental

The chemicals, solvents and experimental techniques used such as elemental analysis, FTIR, ¹H-NMR, solubility study, GPC, DSC, DMA, TGA, mechanical properties (tensile stress, % elongation at break, Young's modulus), water absorption and dielectric properties are already discussed in Chapter 2.

5C.3 General synthesis of Poly(imide siloxane)s from bisphenol-A-di(phthalic anhydride)

The polymerization reactions were conducted by the reaction of BPADA and two different diamines in a random fashion. In all the syntheses, 1 mole of BPADA and mixture of two diamines which add up to 1 mole is presented in the subscript of all the polymer structures respectively. The reactions were conducted under constant flow of nitrogen. A representative polymerization procedure with 5% loading of APPS is as follows.

In a 50 mL, 3 necked round-bottomed flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with 0.655 g (1.259 mmol) BPADA, 0.769 g (1.172 mmol) of 4,4'-bis (3"-trifluoromethyl-*p*-aminobiphenyl ether)biphenyl, and APPS 0.075 g (0.087 mmol) and 20 mL of 1,2-dichorobenzene. The reaction temperature was raised slowly from room temperature to 180 °C. During the reaction, the solution was observed to turn viscous. The reaction was continued for 6 h at 180 °C under nitrogen. The resulting viscous polymeric solution was then cooled to room temperature and was precipitated in 500 mL methanol.

The fibrous product obtained was dried and dissolved in 20 mL dichloromethane and re-precipitated from methanol. The products were dried at 120 °C for 5 h under vacuum and were used for further analysis. The reaction scheme and polymer structures are shown in Scheme 5C.1. A weighed quantity of polymers was dissolved in a measured amount of dichloromethane (15 wt%) and was poured in flat bottom Petri dishes to obtain polymer films. The Petri dishes were covered and the solvent was allowed to evaporate at a controlled rate at 30 °C over night. The Petri dishes were then kept in a vacuum oven and the temperature of the oven was slowly raised to 120 °C and kept under continuous vacuum for 5-6 h to remove any trace of solvent.



Scheme 5C.1: Reaction scheme and structures of the poly(imide siloxane)s with variation of 5 – 40 wt% siloxane loading

5C.4 Characterization

5C.4.1 Poly (imide siloxane) - 2b_{5wt% APPS}



Analalytical calculation for $(C_{68.2147} H_{45.5783} F_{5.58} O_{8.5044} N_2 Si_{0.7113})_n (1155.47 gmol^{-1})_n : C, 70.90; H, 3.97; N, 2.42 Found : C, 71.22; H, 3.72; N, 2.59.$

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2962(-CH₃ group present in APPS); 1776 and 1716 (asymmetric and symmetric –CO- stretching); 1602 (C=C ring stretching); 1506 (band due to C-F stretching); 1389 (asymmetric C-O-C stretching); 1083, 1020 (Si-O-Si stretching); 801 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 7.95 - 7.04 (35.82H), 3.62(s, 0.22H, -CH₂-N<), 1.76(s, 6.27H,-CH₂-), 0.91 - 0.54(s, 0.22H, -CH₂-Si), 0.005 - 0.14(m, 4.09H, Si-CH₃).

5C.4.2 Poly (imide siloxane) - 2b10wt% APPS



Analalytical calculation for $(C_{67.4125} H_{49.2344} F_{5.16} O_{9.0197} N_2 Si_{1.4382})_n (1170.14 gmol⁻¹)_n : C, 69.19; H, 4.24; N, 2.39 Found : C, 69.72; H, 4.03; N, 2.63.$

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2962(-CH₃ group present in APPS); 1773 and 1720 (asymmetric and symmetric –CO- stretching); 1602 (C=C ring stretching); 1504, (band due to C-F stretching); 1389 (asymmetric C-O-C stretching); 1080, 1015 (Si-O-Si stretching); 800 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 7.95 – 7.00(35.15H), 3.62(s, 0.52H, -CH₂-N<), 1.76(s, 6.55H,-CH₂-), 0.91 – 0.54(s, 0.44H, -CH₂-Si), 0.002 – 0.14(m, 7.78H, Si-CH₃).

5C.4.3 Poly (imide siloxane) - 2b_{15wt% APPS}



Analalytical calculation for $(C_{66.5897} H_{52.9839} F_{4.72} O_{9.5482} N_2 Si_{2.1836})_n (1185.19 gmol^{-1})_n$: C, 67.48; H, 4.50; N, 2.36 Found : C, 67.79; H, 4.32; N, 2.72.

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2961(-CH₃ group present in APPS); 1775 and 1716 (asymmetric and symmetric –CO- stretching); 1602 (C=C ring stretching); 1506, (band due to C-F stretching); 1392 (asymmetric C-O-C stretching); 1085, 1022 (Si-O-Si stretching); 800 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 7.95 – 7.03(25.16H), 3.61(s, 0.56H, -CH₂-N<), 1.76(s, 6.84H,-CH₂-), 0.87 – 0.54(s, 0.52H, -CH₂-Si), 0.002 – 0.14(m, 9.18H, Si-CH₃).

5C.4.5 Poly (imide siloxane) - 2b_{25wt% APPS}



Analalytical calculation for $(C_{64.8793} H_{60.7785} F_{3.82} O_{10.6469} N_2 Si_{3.7332})_n (1216.48 gmol^{-1})_n : C, 64.05; H, 5.03; N, 2.30 Found : C, 64.22; H, 5.76; N, 2.59.$

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2964(-CH₃ group present in APPS); 1776 and 1720 (asymmetric and symmetric –CO- stretching); 1602 (C=C ring stretching); 1499, (band due to C-F stretching); 1389 (asymmetric C-O-C stretching); 1080, 1016 (Si-O-Si stretching); 802 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 7.95 – 7.04(21.06H), 3.62(s, 0.92H, -CH₂-N<), 1.76(s, 7.44H,-CH₂-), 0.89 – 0.54(s, 0.84H, -CH₂-Si), 0.002 – 0.17(m, 14.96H, Si-CH₃).

5C.4.6 Poly (imide siloxane) - 2b_{30wt% APPS}



Analalytical calculation for $(C_{63.9905} H_{64.8287} F_{3.35} O_{11.2178} N_2 Si_{4.5384})_n (1232.74 gmol^{-1})_n : C, 62.34; H, 5.30; N, 2.27 Found : C, 62.56; H, 5.43; N, 2.39.$

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2961(-CH₃ group present in APPS); 1773 and 1717 (asymmetric and symmetric –CO- stretching); 1600 (C=C ring stretching); 1501, (band due to C-F stretching); 1382 (asymmetric C-O-C stretching); 1085, 1022 (Si-O-Si stretching); 800 (Si-C stretching).

¹**H-NMR (CDCl₃):** δ (**ppm**) 7.95 – 7.04(22.44H), 3.62(s, 0.98H, -CH₂-N<), 1.76(s, 7.76H,-CH₂-), 0.89 – 0.53(s, 0.90H, -CH₂-Si), 0.001 – 0.18(m, 21.80H, Si-CH₃).

5C.4.7 Poly (imide siloxane) - 2b_{35wt% APPS}



Analalytical calculation for $(C_{63,0801} H_{68,9775} F_{2,87} O_{11,8026} N_2 Si_{5,3632})_n (1249.39 gmol^{-1})_n$: C, 60.64; H, 5.56; N, 2.24 Found : C, 60.93; H, 5.27; N, 2.49.

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2962(-CH₃ group present in APPS); 1773 and 1720 (asymmetric and symmetric –CO- stretch); 1610 (C=C ring stretching); 1504, (band due to C-F stretching); 1377 (asymmetric C-O-C stretching); 1080, 1015 (Si-O-Si stretching); 801 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 7.88 - 6.92(19.14H), 3.55(s, 1.45H, -CH₂-N<), 1.69(s, 8.08H,-CH₂-), 0.89 - 0. 46(s, 1.76H, -CH₂-Si), 0.006 - 0.22(m, 22.84H, Si-CH₃).

5C.5 Results and Discussions

5C.5.1 FTIR spectroscopy

The formation of poly (imide siloxane) was confirmed by FTIR spectroscopy. FTIR spectra of the polyimide films show the absorption bands at about 1780 cm⁻¹ (C=O asymmetric stretching), 1730 cm⁻¹ (C=O symmetric stretching), corresponding to imide bands. Strong absorption band at 2961 cm⁻¹ was due to the presence of methyl groups attached to silicon molecules in APPS. No detectable absorption band at 3400-3100 cm⁻¹ corresponding to amide (-NH-) and acid (-OH) stretching and 1660 cm⁻¹ corresponding to amide stretching C=O bond indicating complete imidization. Strong absorption bands at 1090 and 1020 cm⁻¹ (Si-O-Si stretching) and 800 cm⁻¹ (Si-C) was due to the characteristic peaks of the siloxane group.

5C.5.2 ¹H – NMR spectroscopy

¹H-NMR spectra of the polymers did not show any amide or acid protons, indicating full imidization.

The siloxane incorporation in the polymers was calculated from the integrated peak areas of the proton NMR spectra. Table 5C.1 represents the number of aromatic and aliphatic protons calculated from the structures of poly (imide siloxane)s and their ratio and that found from integrated peak areas from proton NMR spectra. In each of the respective cases it is observed that the ratio of aliphatic / aromatic protons found from the integrated peak areas is less than that calculated values from gross molecular structure. It is observed that the poly(imide siloxane)s have been prepared with the view of incorporating 5 - 40 wt% siloxane loading, actual incorporation is found to be less each case.
Polymer	C-aro	C-ali	F-aro	F-ali	C-ali/aro	F-ali/aro	A - Silo %
2b _{5 wt} % APPS	34.48	11.09	35.82	10.88	0.32	0.30	4.71
2b10wt% APPS	32.93	16.30	35.15	15.29	0.49	0.43	8.78
2b _{15wt} % APPS	31.34	21.64	25.16	17.10	0.69	0.68	14.76
2b _{20wt%} APPS	29.69	27.16	34.28	28.56	0.91	0.84	18.21
2b _{25wt%} APPS	28.03	32.74	21.06	24.18	1.16	1.14	24.57
2b _{30wt%} APPS	26.31	38.51	22.44	31.45	1.46	1.40	28.73
2b _{35wt%} APPS	24.55	44.42	19.14	34.12	1.80	1.78	34.50
2b _{40wt%} APPS	22.69	50.68	20.99	42.43	2.23	2.02	36.18

Table 5C.1: Actual incorporation of siloxane in the poly(imide siloxane)s (2b_{5 wt% APPS} - 2b_{40 wt% APPS}) from ¹H-NMR spectra

C-aro = Theoretical number of aromatic protons calculated from structure

C-ali = Theoretical number of aliphatic protons calculated from structure

C (ali/aro) = Theoretical ratio of aromatic/aliphatic protons

F (ali/aro) = Found ratio of aromatic/aliphatic protons calculated from integrated peaks

A-silo (%) = [F(ali/aro)/C(ali/aro)x 40] =Actual wt% incorporation of siloxane in the polymer structure.

5C.5.3 Molecular weight determination of the polymers

The inherent viscosities and molar masses of the poly(imide siloxane)s are shown in Table 5C.2 which indicates high molar masses. The values indicate the formation of high molar mass products.

Polymer	η _{inh} dL/g	M _n (g/mol)	PDI
2b _{5 wt%} APPS	0.36	34300	1.90
2b _{10wt% APPS}	0.35	32400	2.59
2b _{15wt} % APPS	0.47	37600	2.44
2b _{20wt%} APPS	0.541	55900	2.41
2b _{25wt%} APPS	0.52	35200	2.70
2b _{30wt% APPS}	0.33	64700	2.53
2b _{35wt% APPS}	0.45	49400	1.72
2b _{40wt% APPS}	0.339	42000	2.23

Table 5C.2:	Molecular	weight and	PDI of	(2b _{5 wt% APPS} -	- 2b _{40 wt% APPS})
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 η_{inh} , 0.5 weight % solution of poly(imidesiloxane)s in THF at 30 °C M_n = number average molecular weight

PDI = Polydispersity index

5C.5.4 Polymer solubility

The solubilities of the resulting poly (imide siloxane)s were investigated in different organic solvents. Solubility behavior of the polymers in different solvents is presented in Table 5C.3. These polymers exhibited very good solubility in common organic solvents such as and NMP, DMF, DMAc, THF, chloroform, dichloromethane and was observed to be insoluble in DMSO and acetone. Indeed the siloxane loading has a significant role in polymer solubility. Polymers containing higher loading of siloxane was observed to dissolve in different organic solvents in much lesser time than the ones which has lower siloxane incorporation. Siloxane units incorporated into the polyimide backbone increases the chain flexibility contributing to ease of the polymer to solvent attack [2].

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	CH_2Cl_2	Acetone
2b5wt% APPS	+	+	+	-	+	+	+	-
2b10wt% APPS	+	+	+	-	+	+	+	-
2b _{15wt} % APPS	+	+	+	-	+	+	+	-
2b _{20wt} % APPS	+	+	+	-	+	+	+	-
2b _{25wt%} APPS	+	+	+	-	+	+	+	-
2b _{30wt%} APPS	+	+	+	-	+	+	+	-
2b _{35wt%} APPS	+	+	+	-	+	+	+	_
2b _{40wt%} APPS	+	+	+	-	-+	+	+	-

Table 5C.3: Solubilities of (2b_{5 wt% APPS} – 2b_{40 wt% APPS})

+, soluble at room temperature; -, insoluble at reflux

5C.5.5 Glass transition temperature versus polymer structure

The poly (imide siloxane)s exhibited no crystallization or melting transition in DSC measurements. These polymers show glass transition temperature, which indicates amorphous or glassy morphology. DSC curves of the polymers are shown in Figure 5C.1 indicating glass transition temperatures of poly(imide siloxane)s by varying siloxane loading from 5 - 40% respectively. The glass transition temperature T_g values of the synthesized poly(imide siloxane)s are summarized in Table 5C.4. These poly(imide siloxane)s showed a marked decrease in the T_g values as siloxane loading is increased as greater flexibility is generated leading to lower glass transition temperatures. Compared to the homopolymer 2b synthesized from BPADA discussed in Chapter 5A, these poly(imide siloxane)s showed lower glass transition temperature.

Polymer	DSC	T _d (°C)	FW	SiO ₂ %	A-Silo %	SiO ₂ %	SiO ₂ %
	T _g (°C)	in air	g mol ⁻¹	Theo		Cald	TGA-AIR
2b	228	489	1141.10	-	-	-	-
2b _{5 wt} % APPS	203	452	1155.47	3.69	4.71	3.48	3.46
2b10 wt% APPS	183	445	1170.14	7.37	8.78	6.47	6.43
2b _{15 wt} % APPS	162	439	1185.19	11.05	14.76	10.88	10.84
$2b_{20 wt\%}$ APPS	143	437	1200.76	14.75	18.21	13.44	13.42
2b _{25 wt} % APPS	128	434	1216.48	18.41	24.57	18.10	17.88
2b _{30 wt} % APPS	117	431	1232.74	22.09	28.73	21.15	20.93
2b _{35 wt%} APPS	111	422	1249.39	25.75	34.50	25.38	25.29
2b _{40 wt%} APPS	107	418	1267.04	29.53	36.18	26.72	26.64

Table 5C.4: Thermal Properties of the (2b_{5 wt% APPS} - 2b_{40 wt% APPS})

 $T_d = 5\%$ Weight loss temperature

FW = repeat unit weight

 $SiO_2 \%_{Theo} = [(Molecular weight of SiO_2 x Total no. of elemental silicon from FW) / FW] x 100$

- A-Silo % = Actual wt% incorporation of siloxane in the polymer structure
- $SiO_2 \%_{Cald} = Char residue \%$ from NMR analysis = $[SiO_2 \%_{Theo} x A-silo (\%)] / Siloxane wt \% attempted$

 $SiO_2 \%_{TGA-AIR}$ = Char residue left at 600 °C from TGA analyses carried under air atmosphere



Figure 5C.1: DSC plots of (2b_{5 wt% APPS} – 2b_{40 wt% APPS})

5C.5.5 Thermal stability

The thermal properties of the copolymers were evaluated by TGA in air. The TGA thermograms of the polymers are shown in Figure 5C.2 and the thermal properties of the polymers are summarized in Table 5C.4. In general, the polymers showed good thermal stability. The 5% weight loss temperature of the polymers are governed by the siloxane loading. The poly(imide siloxane) with 5 wt% siloxane loading show highest thermal stability in the series. This is obvious because higher wt% of siloxane loading leads to more degradation at a particular temperature. Higher the siloxane loading lower is the decomposition temperature than the corresponding homopolymer 2b discussed in Chapter 5A. Thermal degradation begins at the Si-C bonds of APPS because the bond dissociation energy is lower than that of the other bonds. It is interesting to note the residual masses of the poly(ether imide) and the poly(imide siloxane)s. While no residual masses were left in case of non siloxane analogue 2b at temperature ~ 625 °C, the amount of char residues left for this series of polymers containing 5 – 40 wt% siloxane loading were in accordance to the amount of siloxane incorporated in the polymer backbone.



Figure 5C.2: TGA plots of poly(imide siloxane)s compared with the homopolyimide

As observed from the curves, the homopolymer 2b shows only one step degradation as only decomposition of the aromatic structure comes into play with increase in temperature. However, the copolymers containing siloxane units in the polymer backbone undergo two step degradation. The first step occurs between 380 - 450 °C and the second step occurs between 500 - 600 °C where at the end ~ 625 °C, a white crystalline char residue is left. Increasing amount of siloxane in the copolymer leads to progressively less thermo-oxidatively stable polymer, but to a higher amount of residue. The first degradation step is attributed to the scission of aliphatic linkages in the polymer backbone. The aromatic structure undergoes further degradation at higher temperature resulting to a white crystalline residue which is silica.

Amount of char residue calculated from the gross molecular formula of the polymers and accounting exact siloxane incorporation from ¹H-NMR spectra was

correlated with the char residue obtained from TGA analysis. At a temperature 625 °C the calculated char residues are in good agreement with that obtained from TGA analyses which consist of silica as the main constituent, as APPS on degradation leads to the formation of white crystalline solid silica.

Representative calculation of char residue for poly(imide siloxane) $2b_{15wt\% APPS}$ FW = repeat unit weight = $(C_{66.5897} H_{52.9839} F_{4.72} O_{9.5482} N_2 Si_{2.1836})_n (1185.19 gmol^{-1})_n$ SiO₂ % _{Theo} = [(Molecular weight of SiO₂ x Total no. of elemental silicon from FW) / FW] x 100 = [(60 x 2.1836)/1185.19] x 100 = 11.05

A-Silo % = Actual wt% incorporation of siloxane in the polymer structure = 14.76 SiO₂ % _{Cald} = $[SiO_2 \%$ Theo x A-silo (%)] / Siloxane wt % attempted

 $= [11.05 \times 14.76] / 15 = 10.88$

 $SiO_2 \%_{TGA-AIR} = 10.84$

5C.5.6 Mechanical properties

The mechanical properties of thin poly(imide siloxane) films are shown in Table 5C.5 and Stress – strain plots of the poly(imide siloxane)s are shown in Figure 5C.3. In general, the mechanical properties of the poly (imide siloxane) films were excellent and exhibited tensile strength and modulus of measurable values. The homopolymer 2b is observed to exhibit highest tensile strength of about 93 MPa and lowest elongation at break of 20% while the siloxane containing polymers have been observed to increase elongation at break sequentially with increase in siloxane loading but with lowering of tensile strength which is obvious because extent of flexibility is generated by the plasticization effect of polydimethylsiloxane. Poly(imide siloxane) containing 40 wt% siloxane loading has been observed to show highest elongation at break of 144%.



Figure 5C.3: Stress – strain plots of the poly(imide siloxane)s

Polymer	Tensile strength (MPa)	Elongation at break (%)	Young's Modulus (MPa)
2b	93	20	1440
2b _{5 wt%} APPS	75	24	1344
2b _{10 wt} % APPS	71	25	1320
2b _{15 wt} % APPS	62	31	1265
$2b_{20 wt\%}$ APPS	57	37	1230
2b _{25 wt} % APPS	47	53	1189
2b _{30 wt} % APPS	44	94	1078
2b _{35 wt} % APPS	32	121	925
2b _{40 wt} % APPS	24	144	890

Fable 5C.5: Mechanica	behavior of (2b ₅ ,	wt% APPS - 2b40 wt% APPS)
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5C.5.7 Water absorption study and dielectric behavior

Water absorption study is an important parameter for materials to be used in electronic applications. Water absorption study of the poly(imide siloxane) were done by immersing rectangular pieces of samples (30x10 mm) in double distilled water at 30 °C after taking the initial weight. Final weight was taken after 24 h and % water absorption was calculated. Table 5C.6 shows the water uptake values as low as 0.02% in case of the polymer (2b_{40 wt% APPS}) and are lesser compared to the corresponding homopolymer, 2b. Negligible small water uptake of these polymers is possibly due to the contribution both from fluorine and siloxane sequences into the backbone of the polyimide backbone and amount of water uptake varied with the siloxane incorporation. Higher siloxane loading lead to lesser water uptake than the ones with lesser amount of siloxane loading. The dielectric constant is also observed to decrease with increase in incorporation of siloxane loading in the polymer backbone and is observed to be minimum in case of poly(imide siloxane) containing 40 wt% APPS due to the combined effect of both fluorine as well as siloxane units present in the polymer backbone.

Polymer	Water absorption (%) after 24 hrs	Dielectric constant At 1MHz
2b	0.20	2.80
2b _{5wt% APPS}	0.19	2.76
2b _{10wt%} APPS	0.16	2.73
2b _{15wt% APPS}	0.13	2.69
2b _{20wt% APPS}	0.11	2.63
2b _{25wt%} APPS	0.09	2.59
2b _{30wt% APPS}	0.08	2.54
2b _{35wt% APPS}	0.05	2.48
2b _{40wt% APPS}	0.02	2.43

Table 5C.6: Water absorption and dielectric behavior of (2b_{5 wt% APPS} - 2b_{40 wt% APPS})

5C.5.8 Rheology behavior

Rheology behavior of the poly(imide siloxane)s were investigated at temperature 50 °C higher to their corresponding glass transition temperatures. Flow curves are shown in Figure 5C.4 comparing with the non-siloxane analogue. With increase in siloxane loading lowering in viscosity was observed. The poly(imide siloxane)s showed low melt viscosity and hence good melt processability. At low shear rates, Newtonian behavior is observed while at higher shear rates apparent viscosity decreases typical of non-Newtonian behavior.



Figure 5C.4: Rheological behavior of the poly(imide siloxane)s

5C.6 Conclusion

Several new poly(imide siloxane)s were prepared on reaction of bisphenol-Adi(phthalic anhydride) with trifluoromethyl - substituted diamines with different levels of siloxane loading from 5-40 wt%. The polymers were well characterized by spectroscopy, thermal, mechanical, water sorption, dielectric studies. The synthesized polymers exhibited very good solubility in different organic solvents. The resulting poly (imide siloxane)s were amorphous as reported and reasonable good thermal stability. The polymers showed glass transition temperatures, thermal stabilities, tensile strength, water uptake and dielectric constant which decreased sequentially but with high elongation at break with increase in siloxane loading. Hence, tailoring of properties of the homopoly(ether imide) is possible by incorporating different levels of siloxane and a host of materials with varied properties can be prepared according to the application demand.

5C.7 References

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5D.1 Introduction

There is an enormous commercial success of various copolymers comprised of different combinations of repeating units. Copolymer synthesis offers the ability to tailor the properties of a homopolymer in a desired direction by the introduction of an appropriately chosen second repeating unit. Copolymerization has been used to alter such polymer properties as flexibility, thermal stability, toughness, glass transition temperature, and crystallinity. The magnitudes and direction of the property alterations differ depending on whether statistical, alternating, or block copolymers are involved.

Polyimides are of special interest for their exceptional thermal, mechanical and electrical properties. Because of such outstanding properties they are applicable in a wide range of industrial applications [1,2]. Polyimides modified with a siloxane segment impart unique properties such as good thermal and oxidative stability, low surface energy, low glass transition temperature, high hydrophobicity, high gas permeability and good biocompatibility, improved solubility and processability and low dielectric constant [3-5]. The insertion of fluorine in the form of -CF₃ groups into the polyimide backbone improves the solubility due to the low cohesion energy provided by the fluorinated groups. The bulky -CF₃ groups increase the fractional free volume which reduces the polymer chain-chain interactions and chain packing [6-9]. One of the most interesting compromises between processability and thermal stability is given by imide-siloxane block copolymers [10]. Effective surface modification by PDMS segments has since then been consistently shown in a wide variety of PDMS containing block copolymers, including polystyrene-PDMS diblock and triblock copolymers [11, 12], poly(methylstyrene)-PDMS multiblock and starblock copolymers [13], polysiloxanepolycarbonate block copolymers [14], polyurethane-polysiloxane graft copolymers [15] and poly(imide siloxane) block copolymers among others.

In the present study five new block copoly(imide siloxane)s have been prepared by reacting two different diamines, 4,4'-bis(*p*-aminophenoxy)-3,3"-trifluoromethyl terphenyl (APTTFT) [16] and amino-propyl terminated polydimethylsiloxane (APPS), separately with 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (bisphenol A dianhydride; BPADA). The reactions were conducted by a two pot solution imidization technique. The diamine APTTFT and the dianhydride BPADA composed the hard block

segment while APPS and BPADA composed the soft block segment. The soft and hard blocks of different block lengths were generated by creating different stoichiometric imbalance in two different flasks and the final polymers were obtained by reacting both the blocks together. Different block copoly(imide siloxane)s were prepared on increasing the hard block lengths (DP) from 7 to 12, 18, 23 and 28 and the soft block lengths (DP) from 4 to 6, 8, 10 and 12, respectively as was calculated from Carother's equation. The resulting polymers have been well characterized by NMR, DSC, and DMA techniques. The properties of the block copolymers were compared with the analogous random copolymer $2a_{20 \text{ wt%}}$ APPS (reported in Chapter 5B) and homopolyimide '2a' (reported in Chapter 5A) prepared without APPS.

5D.2 Experimental

The experimental techniques used such as FTIR, ¹H-NMR, ¹³C-NMR, solubility study, GPC, DSC, DMA, TGA, mechanical properties (tensile stress, % elongation at break, Young's modulus), are already discussed in Chapter 2.

5D.3 General synthesis of block poly(imide siloxane) copolymers

5D.3.1 Preparation of soft block segment (S)

The anhydride terminated soft blocks were prepared by the reaction of BPADA with APPS. The exact feed ratios are given in Table 5D.1. A three necked 50 mL round bottom flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with 0.4018 g (0.7719 mmol) BPADA and 6 mL ODCB. The temperature of the reaction mixture was raised to 60 °C to dissolve the BPADA in ODCB and then 0.4006 g (0.4632 mmol) APPS in 2 mL of ODCB was charged. The small glass vial in which APPS was weighed was washed two times by 2 mL ODCB for efficient transfer of APPS. The temperature was raised to 150 °C, the reaction was conducted for 2 h and this soft block was used for the preparation of block copolymer of BL-1. The other soft blocks were also prepared in a similar way but taking different amounts of BPADA and APPS.

5D.3.2 Preparation of hard block segment (H)

The amine terminated hard blocks were prepared by the reaction of BPADA with APTTFT. The exact feed ratios are given in Table 5D.1. A three necked 50 mL round bottom flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with 0.4813 g (0.9248 mmol) BPADA, 0.7161 g (1.2335 mmol) APTTFT and 10 mL ODCB. The temperature of the reaction mixture was raised slowly to 150 °C and reaction was conducted for 2 h; this hard block was used for the preparation of block copolymer of BL-1. The procedure remained the same for the preparation of rest of the hard blocks segments but taking different amounts of BPADA and APTTFT.

Polymer		Hard block		Soft block				
	BPADA (g / mmol)	APTTFT (g / mmol)	r / DP _n (K)	BPADA (g / mmol)	APPS (g / mmol)	r / DP _n (L)		
BL - 1	0.4813 /	0.7161 /	0.74969	0.4018 /	0.4006 /	0.60004		
	0.9248	1.2335	/ 6.99	0.7719	0.4632	/ 4.00		
BL - 2	0.5457/	0.7161 /	0.84997	0.3374 /	0.4006 /	0.71453		
	1.0485	1.2335	/ 12.33	0.6482	0.4632	/ 6.00		
BL - 3	0.5732 /	0.7161 /	0.89286	0.3098 /	0.4006 /	0.77802		
	1.1014	1.2335	/ 17.66	0.5953	0.4632	/ 8.00		
BL - 4	0.5885 /	0.7161/	0.91661	0.2946 /	0.4006 /	0.81829		
	1.1307	1.2335	/ 22.98	0.5660	0.4632	/ 10.00		
BL - 5	0.5984 /	0.7161 /	0.93201	0.2847 /	0.4006 /	0.84670		
	1.1497	1.2335	/ 28.41	0.5470	0.4632	/ 12.04		

 Table 5D.1: Feed ratio for preparation of block copolymers

 and calculated r values and degrees of polymerization

 $r = moles of BPADA / moles of ATTPFT (for hard block) and moles of APPS / moles of BPADA (for soft block); <math>DP_n = (1 + r) / (1 - r)$

5D.3.3 Polymerization

The reactions were designed in such a way that the soft blocks were always kept anhydride rich and accordingly the hard blocks were amine terminated. The soft blocks were prepared by dissolving weighed amount of BPADA in ODCB at 60 °C and APPS was added on to it in a defined sub-stoichiometric amount. The temperature of the reaction mixture was raised to 150 °C and maintained for 2 h. Similarly, the hard blocks were prepared by reacting APTTFT with a sub-stoichiometric amount of BPADA at 150

°C for 2 h. After 2 h of heating the hard and soft block segments separately, the soft block was transferred to the hard block. Some additional amount of ODCB was used to wash the soft block containing flask and this solvent amount was also transferred to the hard block containing flask to avoid any loss. Then the reaction temperature was raised to 180 °C. The reaction was continued for another 4 h. During the course of reaction, water formed due to imidization was removed azeotropically by ODCB and accordingly fresh solvent was added to makeup for the solvent loss to maintain the solid content in the reaction mixture roughly at about 10 wt%. The reaction temperature was brought down to room temperature and the polymer solution was precipitated in 500 mL methanol. The fibrous product obtained was dried and dissolved in 20 mL dichloromethane and reprecipitated from methanol. The products were dried at 120 °C for 5 h under vacuum and were used for further analysis. The reaction scheme and polymer structures are shown in Scheme 5D.1. A weighed quantity of polymers was dissolved in a measured amount of dichloromethane (15 wt%) and was poured in flat bottom Petri dishes to obtain polymer films. The Petri dishes were covered and the solvent was allowed to evaporate at a controlled rate at 30 °C over night. The Petri dishes were then kept in a vacuum oven and the temperature of the oven was slowly raised to 120 °C and kept under continuous vacuum for 5-6 h to remove any trace of solvent.



Scheme 5D.1: Reaction scheme of the preparation of block copolymers of different hard and soft block lengths

N.B. The values K and L were calculated from the stoichiometric imbalance

5D.3.4 Preparation of soft block and hard block segments for NMR analysis

The same procedure as discussed above was adopted for the preparation of soft block and hard block segments; in addition to that the reaction mixture was heated at 180 °C for 4 h to achieve complete imidization. Instead of precipitating out of the product in a non-solvent, the solvent ODCB was removed by vacuum distillation at 80 °C and the product was finally dried under vacuum for overnight at 100 °C. The products were used as such for NMR analysis.

5D.4 Characterization

Poly (imide siloxane) block copolymer characterization



IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching), 2963 (aliphatic C-H stretching), 1780 and 1720 (asymmetric and symmetric C=O of stretching imide), 1610 (C=C ring stretching band), 1501 (band due to C-F stretching), 1388 (asymmetric C-O-C stretching), 1085, 1020 (Si-O-Si stretching); 800 (Si-C stretching).

¹H-NMR (500 MHz, CDCl₃): $\delta = 7.95$ (H20), 7.90 (H6_H), 7.77 (H6_S), 7.75 (H22), 7.68 (H26), 7.44 (H3_H, H15), 7.4 – 7.25 (H3_S, H5_H, H5_S, H10_S), 7.19 (H16), 7.15 (H23), 7.05 (H9_H), 7.01 (H9_S), 3.75 and 3.61 (H_d), 3.63 (H_a), 1.77, 1.755 and 1.74 (H13), 1.68 (H_c), 1.32 (H_e), 0.89 (H_f). 0.56 (H_b), 0.08 (Si(CH₃)₂).

¹³C-NMR (125 MHz, CDCl₃): δ = 167.85 (C1_s), 166.71 and 166.66 (C1_H), 163.82 (C4_H), 163.25 (C4_s), 155.97 (C16), 154.24 (C18), 152.82 (C8_s), 152.68 (C8_H), 147.58 and 147.29 (C11, connecting unit between H and S block), 147.54 (C11_H), 147.33 (C11_s), 138.51 (C25), 135.79 (C21), 134.62 (C2_s), 134.15 (C2_H), 131.62 (C22), 128.70 (C10_H), 128.60 (C10_s), 128.06 (C15), 127.55 (C6_s, C14), 127.47 (C26), 125.7 (C6_H, C20), 125.57 (C7_s), 124.95 (C7_H), 123.19 (quartet, ¹ J_{CF} = 271 Hz, C24), 123.04 (C5_H), 122.31 (C5_s), 122.16 (quartet, C19, ² J_{CF} = 31 Hz), 120.29 (C23), 119.92 (C9_H), 119.84 (C9_s), 119.52 (C16), 111.87 (C3_H), 111.53 (C3_s), 42.51 (C12), 40.87 (C_a), 40.41 (C_d), 30.95 (C13), 22.54 (C_b), 21.91 (C_e), 15.29 (C_c), 11.60 (C_f), 1.09, 0.99 and 0.03 (Si(CH₃)₂). The notation H and S used in the subscripts denote the respective protons and carbon signals from hard and soft blocks.



soft block (S) - prepolymer

The ¹H and ¹³C NMR data of the repeating units correspond to the values given for the final block copolymer. Here, only the data of the anhydride end group are given.

¹H-NMR (500 MHz, CDCl₃): δ = 7.93 (H6'), 7.46 (H5'), 7.39 (H3'), 7.36 (H10'), 7.04 (H9.).

¹³C-NMR (125 MHz, CDCl₃): $\delta = 165.22$ (C4'), 162.57 and 162.08 (C1'), 151.96 (C8'), 148.36 (C11'), 133.94(C2'), 128.95 (C10'), 127.57 (C6'), 124.87 (C5'), 124.21 (C7'), 120.19 (C9'), 112.37 (C3').



hard block (H) - prepolymer

The ¹H and ¹³C NMR data of the repeating unit correspond to the values given for the final diblock copolymer. Here, only the data of the amino end group are given.

¹H-NMR (500 MHz, CDCl₃): δ = 7.89 (H20'), 7.93 (H22'), 6.93 (H16', H23'), 6.71 (H15').

¹³C-NMR (125 MHz, CDCl₃): δ = 156.57 (C18'), 147.70 (C17'), 143.47 (C14'), 138.85 (C25'), 133.92 (C21'), 131.34 (C22'), 127.40 (C26'), 125.75 (C20'), 132.20 (quartet, ¹*J*_{CF} = 271 Hz, C24'), 122.1 (quartet, ²*J*_{CF} = 31 Hz, C19'), 121.42 (C16'), 117.71 (C23'), 116.22 (C15').

5D.5 Results and discussions

5D.5.1 Spectroscopy

The formation of poly(imide siloxane) block copolymers was confirmed firstly by FTIR. The FTIR spectra of the polyimide films show absorption bands at about 1780 cm⁻¹ (C=O asymmetric stretching) and 1720 cm⁻¹ (C=O symmetric stretching), corresponding to the imide bands. The strong absorption band at 2961 cm⁻¹ corresponds to the C-H stretching of the methyl groups attached to silicon in APPS and also corresponds to the C-H stretching of the isopropylidene group coming from the BPADA unit. The strong absorption bands at 1080, 1020 cm⁻¹ (Si-O-Si stretching), and 800 cm⁻¹ (Si-C) are characteristic for the siloxane group.

Further structural confirmation was achieved by NMR studies. ¹H and ¹³C NMR spectra of the polymers were recorded using CDCl₃ as solvent. Representative ¹H NMR spectra of a block copolymer (BL-1), an anhydride-terminated soft block ($L \sim 4$) and of an amine-terminated hard block (K \sim 7) are shown in Figure 5D.1. The spectra confirm the expected structures, i.e., anhydride and amine termination, respectively, for the prepolymers and none of these end groups for the final block copolymers. Both, the ¹H and ¹³C NMR spectra did not show signals corresponding to amide groups indicating complete imidization and supporting the findings in FTIR. It was not possible to calculate the exact block length that was generated in the polymer after the end of the final polymerization in a satisfactory accuracy based on NMR signal integrals. Therefore, to get an idea on block lengths several soft blocks and hard blocks were prepared under similar conditions as the final polymer was prepared. According to the above mentioned equation DP was calculated from r values which were determined from appropriate ¹H NMR signal integrals. The r value for the soft blocks was calculated from the H₆ integral value divided by the total integral of H6 and H6'. The later stands for all initial anhydride groups whereas H6 represents the imide structures and, for full conversion of amine groups, also the number of initial amine groups. For the soft block prepolymers of BL-1 and BL-3 the expected DP values of 4 and 8 could be exactly reproduced. Furthermore, the ratio of propyl end groups and PDMS methyl groups remained unchanged compared with the parent amino-terminated PDMS proving that no degradation of the PDMS occurred. For the hard blocks the r value was calculated from the (H16 + H23) integral value divided by the total integral of H16, H16', H23, and H23'. Here, the later represents all APTTFT units whereas (H16 + H23) stands for the reacted amine groups and is equivalent to the fully converted anhydride groups of BPADA. For the hard block prepolymers of BL-1 and BL-3 slightly higher DP values than expected (9.9 vs. 7 and 19 vs. 17.7) were found. From mathematical point of view it is obvious that for small r values, i.e., for decreasing the stoichiometric imbalance and so for higher DPs, the DP calculation requires very accurate integral values. However, with increasing DP the integration of the decreasing end group signals becomes more inaccurate. Therefore, this method only should apply for the samples with smaller block lengths. In our case, the NMR results were always in good agreement with the calculated values indirectly suggesting that the block lengths for different soft and hard blocks in the final block copolymers should be according to the reaction design (Table 5D.1).



Figure 5D.1: ¹H NMR spectra of the block copolymer (BL-1) (a) of an anhydrideterminated soft block (L ~ 8) (b) and of an amine-terminated hard block (K ~ 7) (c) Characteristic anhydride and amine end group signals are marked by • and ■, respectively

5D.5.2 Polymer solubility

The solubility of the resulting poly(imide siloxane)s was investigated in different organic solvents. The results are presented in Table 5D.2. All block polymers exhibited very good solubility in common organic solvents such as N-methyl-2-pyrrolidinone (NMP), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc), tetrahydrofuran (THF), chloroform (CHCl₃) and dichloromethane (CH₂Cl₂), and were observed to be insoluble in dimethyl sulphoxide (DMSO) and acetone.

5D.5.3 Molecular weight determination of the polymers

GPC molecular weights of the poly(imide siloxane)s shown in Table 5D.2 indicate formation of high molar mass products. As the overall stoichiometric imbalance is the same when one considers the total amount of amines (APPS and APTTFT) and anhydrides (BPADA) used for the generation of block copolymers (Table 1), the development of molar masses (Table 5D.2) in all the block copolymers is comparable within the range of experimental error.

Polymer	M _w (g/mol)	PDI	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	CH ₂ Cl ₂	Acetone
BL-1	68800	1.79	+	+	+	-	+	+	+	-
BL-2	79300	1.86	+	+	+	-	+	+	+	-
BL-3	70400	1.88	+	+	+	-	+	+	+	-
BL-4	76000	1.95	+	+	+	-	+	+	+	-
BL-5	79000	1.96	+	+	+	-	+	+	°+	-

Table 5D.2: GPC molecular weights and solubility of the block copolymers

M_w = weight average molecular weight by GPC; PDI = polydispersity index; +soluble at room temperature; -, insoluble at reflux.

5D.5.4 Glass transition temperature versus polymer structure

The final poly(imide siloxane)s block copolymers exhibited no crystallization or melting transition in DSC measurements. These polymers show glass transition

temperatures, which indicate amorphous or glassy morphology. DSC curves of the block polymers are shown in Figure 5D.2. The glass transition temperature values are summarized in Table 5D.3. An increasing trend of glass transition temperature of the hard blocks is observed with increasing hard block lengths in the polymers with a reproducibility of \pm 1K. The T_g of the soft blocks did not show a clear tendency and the reproducibility of the values is only about \pm 5K. The DMA T_g values of the hard blocks are plotted against their block length in Figure 5D.3 and confirm the linear dependency of the DSC results. It is interesting to note from Table 5D.3 that there is a considerable increase in Tg values by 40 K of the block copolymer BL-1 in comparison to the analogous random copolymer with a siloxane loading of 20 wt% (2a_{20 wt% APPS}). This difference increases further as the block length of the hard block increases and for the block copolymer BL-5 the DSC T_g value approaches the T_g value of the corresponding homopolyimide '2a'. This rise in hard bock Tg values in the block copolymers may be due to greater structural regularity generated which leads to a better micro phase separation and hence a higher Tg value obtained compared to the randomly segmented polymer.



Figure 5D.2: DSC curves of the block copoly(imide siloxane)s



Figure 5D.3: Tg of hard blocks in dependence on the hard block length

5D.5.5 DMA measurements

Dynamic mechanical analyses of the samples of thickness around 300 microns were recorded to get an idea on the T_g values and changes in modulus of the polymers with temperature. The T_g 's taken from the tan ∂ peaks at 10 Hz are given in Table 5D.3. These values show the same raising trend in T_g values like the DSC measurements. However, the DMA T_g values are higher by 25-30 °C than the DSC T_g values which is a common effect. Also, with increase in the soft block length the storage modulus shows a decreasing trend. This may be due to greater flexibility generated on increasing the soft block length.

5D.5.6 Thermal stability

The thermal properties of the copolymers were evaluated by TGA. The TGA thermograms of the polymers are shown in Figure 5D.4 and the thermal properties of the polymers are summarized in Table 5D.3. The 5% weight loss temperature of these polymers is around 470 °C indicating good thermal stability which is increased by 20 K compared to the corresponding random copolymer $2a_{20} G_{Mt\% APPS}$. This can be attributed to the formation of rather long aromatic imide building blocks (hard blocks) in the block copolymers that provide higher thermal stability. However, there is no effect on the

thermal stability of the block copolymers as the hard block length increases. The block copolymers were thermally less stable than the homopolyimide without siloxane moiety. All these polymers showed high char residues of more than 45-47 wt% at 750 °C under nitrogen atmosphere. It is interesting to note that the random copolymer is thermally less stable than the block copolymers but the char residue in both cases is the same. The homopolyimide '2a' provides higher char residue in comparison to siloxane loaded block and random copolymers. This is attributed to the fact that the siloxane moieties are thermally more labile and are prone to degradation.



Figure 5D.4: TGA thermograms of the block copoly(imide siloxane)s

Polymer	DSC /	$T_{g}(^{o}C)$	DMA (tan ∂)	Temp. at 5% Weight loss	Residue at 750 °C	
	Soft block	Hard block		T _d (°C)	(%)	
2a _{20 wt} % APPS	-	132	146	452	45	
BL-1	5	173	200	472	45	
BL-2	12	174	203	468	47	
BL-3	2	186	210	468	45	
BL-4	6	188	213	469	46	
BL-5	2	194	218	470	45	
2a	-	216	210	519	62	

Table 5D.3: Thermal properties of the poly(imide siloxane) block copolymers

5D.5.7 Mechanical properties

Mechanical properties of the block copolymers were measured from solution cast thin films. For better comparison of the properties also a random copolymer was prepared and was tested under similar conditions. Dog-bone specimens with a parallel length of 25 mm and a width of 4 mm were produced by punching. The mean thickness of the specimen was between 0.04 and 0.27 mm, it varied by up to about \pm 10% along the specimen. This is one of the reasons of a remarkable scatter in the mechanical values. For each block copolymer sample 5 specimens were investigated with different thickness. Most of the samples failed before the neck run over the whole parallel length of the specimen. Disregarding some outliers the modulus, yield stress as well as stress and strain at break together with the variances of these values are summarized in Table 5D.4.

All modulus and yield stress values of the block copoly(imide siloxane)s are in the same range with slightly higher values for BL-1 and BL-2. For each sample there was at least one specimen, which broke before reaching the mean strain at break. The random copolymer has a clearly lower yield stress and none of the 4 tested specimen yielded clearly, all specimen failed shortly after the yielding point. In comparison to the homopolyimide (stress at break 73 MPa and strain at break 9.8%), the block copolymers showed lower stress at break but high strain at break.

Properties	BL-1	BL-2	BL-3	BL-4	BL-5	2a _{20 wt%} APPS
Tensile modulus[MPa]	1943	2001	1861	1829	1831	1821
Variance	12.3%	11.9%	10.9%	10.0%	11.9%	8.4%
Yield stress [MPa]	54	53.8	49.4	51.6	51.6	45.3
Variance	7.5%	5.5%	4.6%	9.7%	5.3%	3.1%
Stress at break [MPa]	49.0	49.9	49.8	48.9	49.8	42.2
Variance	11.2%	9.4%	9.5%	9.1%	11.4%	3.6%
Strain at break [%]	91.5	84.3	75.3	72.8	81.3	7.9
Variance	2.3%	10.1%	2.3%	4.9%	8.9%	27.5%

5D.6 Conclusion

Five new block copoly(imide siloxane)s of different soft and hard block lengths were prepared by reacting two different diamines, APTTFT and APPS, separately with BPADA by two pot solution imidization technique. The anhydride terminated soft and amine terminated hard blocks of different block lengths were generated by creating different stoichiometric imbalance in two different pots. The individual block lengths were calculated from NMR results and revealed a very reliably good correlation with the calculated block lengths for the products with low degree of polymerization. Both, DSC and DMA tan δ results indicate that as the block length increases the hard block glass transition temperature of the respective polymers increases, too Therefore, the formation of block structure is directly indicated by the raise in glass transition temperature by 40 K of the polymer BL-1 with hard block degree of polymerization of 7 in comparison to the random copolymer (DSC T_g 132 °C). The block copolymer (BL-5) with the hard block degree of polymerization of 28 showed with Tg = 194 °C a very high glass transition temperature in the range of that of the homopolyimide without APPS. The formation of different block lengths has also consequences on the final storage modulus of the block copolymers, which decreases as the soft block lengths increases. But the block copoly(imide siloxane)s show higher yield stress than the corresponding random copolymers and the strain of break is also about 10 times higher not only as that observed in the random copolymers but also compared to that of the homopolyimides. This demonstrates nicely how important it can be to fine-tune the block structure in segmented block copolymers in order to optimize the materials properties.

5D.7 References

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CHAPTER 6A

NOVEL FLUORINATED POLY(ETHER IMIDE)S DERIVED FROM ANTHRACENE MOIETY

6A.1 Introduction

Aromatic polyimides have been of great technological importance due to their outstanding thermal and electrical properties [1, 2]. However, their applications have been limited in many fields because aromatic polyimides are normally insoluble in common organic solvents and have extremely high glass transition or melting temperatures, which preclude melt processing. Hence, one of the drawbacks in using aromatic polyimides is their poor processability, and a great deal of effort has been made to improve the processing characteristics of these intractable polyimides [3, 4]. One of the successful approach to improve the solubility and processability of polyimides with minimum detrimental effect on their thermal stability is the introduction of pendent trifluoromethyl groups ($-CF_3$) in the polymer backbone [5, 6]. Hence, the search for new dianhydrides and diamines required for the synthesis of polyimides is ever on an increase. A new diamine monomer TFAA synthesized is already discussed in Chapter 3 is utilized with five commercially available dianhydrides namely pyromellitic dianhydride (PMDA), 4,4'-(Hexafluoro-isopropylidene)diphthalic anhydride (6FDA), 3, 3', 4, 4'benzophenone tetracarboxylic dianhydride (BTDA), o-diphthalic anhydride (ODPA), bis phenol-A- di(phthalic anhydride) (BPADA) to synthesize new poly(ether imide)s. During synthesis of the diamine monomer, violet fluorescence was observed in a solution of toluene. Hence, our interest was focused to study if any light emitting properties existed in case of the newly synthesized poly(ether imide)s because light-emitting polymers have many potential advantages, than the conventional light emitting materials[7].

6A.2 Experimental

The chemicals, solvents and experimental techniques used such as elemental analysis, FTIR, ¹H-NMR, solubility study, DSC, DMA, TGA, mechanical properties (tensile stress, % elongation at break, Young's modulus), water absorption and light properties(UV and PL) are already discussed in Chapter 2.

6A.3 General synthesis of Polyimides from 9, 10 - bis (3"- trifluoromethyl – paminobiphenyl ether) anthracene

of new diamine monomer 9,10-bis[3'-trifluoromethyl-4'(4"-**Synthesis** aminobenzoxy) benzyl]anthracene (TFAA) is already discussed in Chapter 3. The diamine monomer led to a number of new fluorinated polyimides by thermal imidization route when reacted with different commercially available dianhydrides like PMDA, 6FDA, BTDA, ODPA and BPADA. All polymerization reactions were carried out under constant nitrogen flow. An equimolar amount of diamine and dianhydride monomers were used for the synthesis of the polyimides. A representative polymerization procedure is as follows. A 50 mL round-bottomed flask equipped with nitrogen inlet and a magnetic stirrer was charged with 0.56 g (0.833 mmol) of TFAA, 0.43 g (0.833 mmol) of BPADA and 10 mL DMF was added in the flask. The resulting solution was stirred for 30 minutes at room temperature. The poly (amic acid) solution was cast onto clean and dry glass Petri dishes. The films were dried in vacuum oven at 80 °C overnight followed by 100, 150, 200, 250 °C for 1 h at each temperature and 300 °C for 30 minutes and at 350 °C for 15 minutes under nitrogen flow. Polyimide films were then removed by immersing the glass plates in boiling water. Scheme 6A.1 shows the reaction scheme and structure of the polymers.



Scheme 6A.1: Reaction scheme and structure of the poly(ether imide)s from TFAA

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6A.4 Characterization

6A.4.1 Poly(ether imide) 3a



Analytical Calculation for $(C_{50} H_{24} O_6 F_6 N_2)_n$ (862.756 gmol⁻¹)_n: C, 69.60%; H, 2.80%; N, 3.24%; Found: C, 68.51%; H, 2.52%; N, 3.34%.

IR (KBr) (cm⁻¹): 3068, 1786, 1734, 1614, 1503, 1435, 1380, 1239, 1186, 1055, 1015, 881, 723, 686.

6A.4.2 Poly(ether imide) 3b



Analytical Calculation for $(C_{58} H_{28} O_6 F_{12} N_2)_n$ (1076.876 gmol ⁻¹)_n: C, 64.69%; H, 2.62%; N, 2.60%; Found: C, 65.23%; H, 2.23%; N, 2.92%.

IR (KBr) (cm⁻¹): 3069, 1786, 1734, 1614, 1503, 1485, 1380, 1259, 1139, 1055, 882, 722, 691.

¹H-NMR (CDCl₃): δ (ppm) 8.09 (d, J = 8Hz, 2H), 7.98 (s, 2H), 7.92 (d, J = 8Hz, 2H), 7.81(s, 2H), 7.67 (d, J = 6.6Hz, 4H), 7.63(d, 6.5Hz, 2H), 7.54(d, J=8Hz, 4H), 7.45(d, 5.5Hz, 4H), 7.37(d, J = 8.5Hz, 4H), 7.33(d, J = 6Hz, 2H).

6A.4.3 Poly(ether imide) 3c


Analytical Calculation for (C₅₇ H₂₈ O₇F₆N₂)_n (966.865 gmol⁻¹)_n: C, 70.80%; H, 2.91%; N. 2.89%; Found: C, 70.91%; H, 2.46%; N, 2.92%.

IR (KBr) (cm⁻¹): 3495, 3069, 1786, 1734, 1614, 1503, 1485, 1380, 1259, 1139, 1055, 882, 722, 691.

¹H-NMR (CDCl₃): δ (ppm) 8.33 (s, 2H), 8.29 (d, J = 6.85Hz, 2H), 8.18 (d, J = 6.85 Hz, 2H), 7.82(s, 2H), 7.67 (d, J = 8.4 Hz, 4H), 7.62(d, J = 3Hz, 2H), 7.57(d, J = 7.5 Hz, 4H), 7.44(d, J = 7.6Hz, 4H), 7.38(d, J = 7.5Hz, 4H), 7.31(d, J = 8Hz, 2H).

6A.4.4 Poly(ether imide) 3d



Analytical Calculation for $(C_{56} H_{28} O_7 F_6 N_2)_n$ (942.847 gmol⁻¹)_n: C, 71.33%; H, 2.99%; N, 2.97%; Found: C, 71.53%; H, 2.83%; N, 3.13%.

IR (KBr) (cm⁻¹): 3069, 1786, 1730, 1614, 1506, 1485, 1378, 1259, 1139, 1055, 882, 722, 686.

¹**H-NMR (CDCl₃):** δ (ppm) 8.05 (d, J = 8.5Hz, 2H), 7.80 (s, 2H), 7.68 (d, J = 3Hz, 2H), 7.67(d, J = 3Hz, 2H), 7.63 (d, J = 6.5Hz, 2H), 7.60(s, 2H), 7.56(s, 2H), 7.55(s, 2H), 7.45(d, J = 7Hz, 4H), 7.37(d, J = 8.5Hz, 4H), 7.32(d, 7Hz, 4H).

6A.4.5 Poly(ether imide) 3e



Analytical Calculation for (C₇₁ H₄₂ O₈F₆N₂)_n (1165.131 gmol⁻¹)_n: C, 73.19%; H, 3.63%; N, 2.40%; Found: C, 73.53%; H, 3.13%; N, 2.78%.

IR (KBr) (cm⁻¹): 3053, 2969, 1778, 1734, 1618, 1507, 1444, 1378, 1333, 1247, 1136, 1055, 882, 722, 682.

¹H-NMR (CDCl₃): δ (ppm) 7.91 (d, J = 8Hz, 2H), 7.79 (s, 2H), 7.68 (d, J = 3Hz, 2H), 7.66(d, J = 3Hz, 2H), 7.60 (s, 2H), 7.52(d, 8Hz, 4H), 7.45(s, 4H), 7.43(s, 2H), 7.38 – 7.34(m, 10H), 7.30(d, J = 8Hz, 2H), 7.05(d, J = 8Hz, 4H), 1.77(s, 6H).

6A.5 Results and discussions

6A.5.1 FTIR spectroscopy

The formation of the poly(ether imide)s were confirmed by FTIR spectra which showed absorption bands at about 1786 cm⁻¹ (C = O asymmetric stretching), 1734 cm⁻¹ (C = O symmetric stretching), 1380 cm⁻¹ (C - N stretching), and 721 cm⁻¹(C = O bending) which are characteristic of the imide rings. Absence of absorption bands at 1720 cm⁻¹ corresponding to C = O stretching of carboxylic acid and at 1660 cm⁻¹ corresponding to C = O amide stretching indicating complete imidization.

6A.5.2 ¹H-NMR spectroscopy

¹H-NMR spectra of the polymers did not show any amide or acid protons, indicating full imidization. ¹H-NMR of Poly (ether imide) 3a was not possible to record due to its insolubility at room temperature in any of the suitable solvents used for NMR spectroscopy. However, ¹H-NMR spectra were recorded for 3b, 3c, 3d and 3e and are shown below in Figures 6A.1– 6A.4. It reveals good matching of integrated peaks for chemically different protons arising from different polymers.











Figure6A.3: ¹H-NMR spectrum of Poly(ether imide) 3d



Figure 6A.4: ¹H-NMR spectrum of Poly(ether imide) 3e

6A.5.3 Polymer solubility

The solubilities of the resulting poly(ether imide)s were investigated in different organic solvents. The solubility behavior of the poly(ether imide)s and inherent viscosity values are presented in Table 6A.1. The poly(ether imide)s exhibited good solubility in common organic solvents except 3a. All the polymers except 3a are soluble in chloroform at room temperature and hence viscosity is measured using chloroform as solvent. The poly(ether imide) 3a is soluble only in NMP on heating. Polymers 3b, 3c, 3d and 3e are soluble in other solvents such as DMF, DMAc, DMSO and THF on heating. All the polymers are observed to be insoluble in acetone.

Polymer	η (dL / g)	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	Acetone
3a		+	-	-	-	-	-	_
3b	0.35	+	+	+	+	. +	++	-
3c	0.36	+	+	+	+	+	++	-
3d	0.39	+	+	+	+	+	++	-
3e	0.59	+	+	+	+	+	++	-

Table 6A.1: Solubilities of the Poly(ether imide)s from TFAA

++, soluble at room temperature; +, soluble on heating; -, insoluble at reflux

6A.5.4 Thermal properties

The thermal properties of the poly(ether imide)s were evaluated by DSC and TGA. The thermal properties of the polymers are summarized in Table 6A.2. The polymer did not exhibit crystallization or melt transition in DSC measurements. The T_g observed follows the trend 3a (330 °C) > 3b (315 °C) > 3c (309 °C) > 3d (300 °C) > 3e (256 °C). Representative DSC plots of the polymers are shown in Figure 6A.5. Glass transition temperatures of the polymers depend on many factors such as polymer symmetry, intermolecular force and rigidity of polymer backbone [8]. The PMDA based polyimide (3a) showed highest T_g than other dianhydride based polymers, which can be explained on the basis of rigid PMDA moieties in the polyimides backbone. The higher T_g value of 6FDA based polymer (3b) in comparison to BTDA based polymer (3c) is expected because of the presence of bulky 6F unit in the polymer backbone and the same trend was observed. The next higher glass transition temperature is observed in case of ODPA based polyimide (3d) followed by the polyimide based on BPADA (3e). The polymer 3e that showed lowest T_g in the series which is attributed to the presence of more numbers of flexible ether linkages in the polymer backbone. The 5% weight loss temperature of these polymers is in the range of 502 – 552 °C under nitrogen (Figure 6A.6) which indicates good thermal stability.

Table 6A.2: Thermal properties of the poly(ether imide)s from TFAA

Polymer	DSC Tg °C	T _{d,5} (°C)	T _{d,10} (°C)	Char residue at 800 °C in N ₂
3a	330	552	579	65.42
3b	315	528	550	61.34
3c	309	538	574	62.83
3d	300	525	557	61.80
3e	256	502	543	65.71

 $T_{d,5} = 5\%$ Weight loss in N₂; $T_{d,10} = 10\%$ Weight loss in N₂



Figure 6A.6: TGA plots of poly(ether imide)s 3a - 3e

6A.5.5 Mechanical properties

The mechanical properties of the poly(ether imide) films prepared are summarized in Table 6A.3. The polymers exhibited high tensile strength upto 80 MPa and elongation at break of upto 10%. The Young's modulus of the polymers was as high as 3.2 GPa measured at 30 °C. The mechanical properties of the polymer 3a could not be measured as the film was brittle.

Polymer	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at Break (%)
	-	-	-
3b	40	2.33	4.9
3c	80	3.20	8
3d	74	2.90	10
3e	70	2.62	9

Table 6A.3 Mechanical properties of the poly(ether imide)s 3a - 3e

6A.5.6 Optical properties

From the spectra of the polymers obtained from UV-VIS spectrophotometer it is observed that with the decrease in wavelength, absorbance gradually increases and it reaches maximum at 520, 527, 467, 441 and 453 nm for the polymers 3a, 3b, 3c, 3d and 3e respectively. The optical properties are tabulated in Table 6A.4. Figure 6A.7 (i) shows the UV-VIS spectra of the polymers. The corresponding energy values in electron volts (eV) can be the band gap of the materials, which lies in the visible range of the electromagnetic spectrum (1.55 - 3.10 eV). From photoluminescence spectra as observed from Figure 6A.7 (ii) the flat peak centering is at 530, 600, 523 and 480 nm for the polymers 3b, 3c, 3d and 3e respectively, however, no such peak has been observed for polymer 3a although it is observed in UV-VIS spectra. A shoulder is also observed at 610 nm for the polymer 3b due to defect transition. The band gap energy values obtained from the PL spectra are in close agreement as that obtained from UV spectra. So these polymer materials may be used for light emitting purpose.

Polymer	Peak Wavelength (nm) from UV	Color from EM spectrum	Band Gap energy (eV)	Peak Wavelength (nm) from PL	Band Gap energy (eV)	Color from EM spectrum
3a	520	Green	2.38	-	-	-
3b	527	Green	2.35	530 / 610	2.33	Green/ Yellow
3c	467	Blue	2.65	600	2.06	Orange
3d	441	Violet	2.81	523	2.37	Green
3e	453	Blue	2.73	480	2.58	Blue

Table 6A.4: Optical properties of the poly(ether imide)s



(i)





6A.6 Conclusion

A new diamine monomer have been synthesized which led to several novel fluorinated polyimides by thermal imidization when reacted with different dianhydrides. The synthesized polymers mainly 3b, 3c, 3d and 3e exhibited good solubility in different organic solvents. The resulting poly(ether imide)s exhibited good thermal stability under nitrogen. These polymers showed good mechanical strength and Young's modulus and very high T_g . The polymers showed energy values which may be the band gap of the materials and they are found to lie in the visible range of the electromagnetic spectrum. These polymers may find application as light emitting polymers.

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CHAPTER, 6B

NOVEL FLUORINATED POLY(IMIDE SILOXANE)S DERIVED FROM ANTHRACENE MOIETY

6B.1 Introduction

Aromatic polyimides are of great technological importance due to their outstanding thermal and electrical properties [1, 2]. However, their applications have been limited in many fields because they are normally insoluble in common organic solvents and they have extremely high glass transition or melting temperatures, which preclude melt processing. One of the successful approaches to improve the solubility and processability of polyimides with minimum detrimental effect on their high thermal stability is the introduction of pendent trifluoromethyl groups (-CF₃) in the polymer backbone [3, 4]. Incorporation of both -CF₃ groups and siloxane units in the polymer backbone leads to dramatic improvement in solubility with minimum moisture uptake and lowering of the dielectric constant. In the present work we have incorporated siloxane units into the respective homopolyimides (3a - 3e) reported in Chapter 6A. The diamine monomer (TFAA) and the same series of dianhydrides PMDA, 6FDA, BTDA, ODPA and BPADA were coupled with 40 wt% amino-propyl terminated polydimethylsiloxane (APPS) for the synthesis of poly (imide siloxane) segmented copolymers. Solubility, spectroscopic characteristics, as well as thermal, mechanical and dielectric properties have been reported in this investigation.

6B.2 Experimental

The experimental techniques used such as FTIR, ¹H-NMR, solubility study, GPC, DSC, DMA, TGA, mechanical properties (tensile stress, % elongation at break, Young's modulus), water absorption and dielectric properties are already discussed in Chapter 2.

6B.3 General synthesis of Poly(imide siloxane) copolymers from TFAA

The polymerization reactions were conducted by the reaction of each of the dianhydrides - PMDA, 6FDA, BTDA, ODPA and BPADA with two different diamines in a random fashion. The reactions were conducted under constant flow of nitrogen. The polymers $3b_{40 \text{ wt\%} \text{ APPS}}$, $3d_{40 \text{ wt\%} \text{ APPS}}$, $3e_{40 \text{ wt\%} \text{ APPS}}$ were synthesized by one-pot solution imidization method. A representative polymerization procedure of $3b_{40 \text{ wt\%} \text{ APPS}}$ is as follows:

A 50 mL, 3 necked round- bottomed flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with 0.722 g (1.626

mmol) 6FDA, 0.476 g (0.699 mmol) TFAA and 0.80 g (0.927 mmol) of APPS and 20 mL of 1,2-dichorobenzene were added with stirring. The temperature was raised slowly from room temperature to 180 °C. During the reaction, the solution was observed to turn viscous. The reaction was continued for 6 h at 180 °C under nitrogen. The resulting viscous polymer solution was then cooled to room temperature and was precipitated from methanol. The fibrous product obtained was dried and dissolved in 20 mL dichloromethane and re-precipitated from methanol. The products were dried at 120 °C for 5 h under vacuum and were used for further analysis. The reaction scheme and polymer structures are shown in Scheme 6B.1. A weighed quantity of polymers was dissolved in a measured amount of dichloromethane (15 wt%) and was poured in flat bottom Petri dishes to obtain polymer films. The Petri dishes were covered and the solvent was allowed to evaporate at a controlled rate at 30 °C over night. The Petri dishes were then kept in a vacuum oven and the temperature of the oven was slowly raised to 120 °C and kept under continuous vacuum for 5-6 h to remove any trace of solvent. Transparent pale - yellowish colored films were obtained in all three polymers 3b40 wt% APPS, 3d_{40 wt% APPS}, and 3e_{40 wt% APPS} respectively. Scheme 6B.1 shows the reaction scheme and structure of the polymers $3b_{40 \text{ wt\% APPS}}$, $3d_{40 \text{ wt\% APPS}}$ and $3e_{40 \text{ wt\% APPS}}$.

The $3a_{40 \text{ wt\% APPS}}$ and $3c_{40 \text{ wt\% APPS}}$ was synthesized by thermal imidization route as the polymer solution was observed to be inhomogeneous when one-pot solution imidization was followed. A representative polymerization procedure of $3a_{40 \text{ wt\% APPS}}$ is as follows:

A 50 mL round-bottomed flask equipped with nitrogen inlet and a magnetic stirrer was charged with 0.746 g (1.097mmol) of TFAA, 0.445 g (2.031 mmol) of PMDA, 0.808 g (0.934 mmol) of APPS and 10mL of dry DMF was added. The resulting solution was stirred for 30 minutes at room temperature. The poly (amic acid) solution was cast onto clean and dry glass petri dishes. The films were dried in vacuum oven at 80 °C overnight followed by 100, 150, 200, 250 °C for 1 h at each temperature and 300 °C for 30 minutes and at 350 °C for 15 minutes under slow stream of nitrogen flow. Poly(imide siloxane) films were then removed from the substrate by immersing the glass plates in boiling water.



Scheme 6B.1: Reaction scheme and structure of the poly(imide siloxane)s from TFAA

6B.4 Characterization

6B.4.1 Poly(imide siloxane) - 3a40 wt%APPS



Analytical calculation for $(C_{43.8452}H_{47.8556}O_{9.3626}F_{3.24}N_2Si_{4.7426})_n$ (947.458 gmol⁻¹)_n: C, 55.58%; H, 5.09%; N, 2.95%; Found: C, 55.25%; H, 5.21%; N, 2.83%.

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2963(-CH₃ group present in APPS); 1777 and 1720 (asymmetric and symmetric -CO- stretching); 1610 (C=C ring stretching); 1506 (band due to C-F stretching); 1388 (asymmetric C-O-C stretching); 1083, 1022 (Si-O-Si stretching); 801 (Si-C stretching).

6B.4.2 Poly (imide siloxane) - 3b40 wt%APPS



Analytical calculation for $(C_{51.3734}H_{57.5602}O_{10.1667}F_{8.58}N_2Si_{5.8767})_n$ (1193.844 gmol⁻¹)_n: C, 51.68%; H, 4.86%; N, 2.34%; Found: C, 51.33%; H, 4.73%; N, 2.52%.

IR (KBR) (cm⁻¹): 3069 (aromatic C-H stretching); 2961(-CH₃ group present in APPS); 1776 and 1717 (asymmetric and symmetric –CO- stretching); 1609 (C=C ring stretching); 1506 (band due to C-F stretching); 1392 (asymmetric C-O-C stretching) ; 1085, 1021 (Si-O-Si stretching); 800 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 7.97-7.04(18.58H), 3.72(s, 2.28H, -CH₂-N<), 1.69(s, 2.28H, -CH₂-), 0.89-0.57(m, 3.36H, -CH₂-Si), 0.18-0.02(m, 38.68H, Si-CH₃).

6B.4.3 Poly (imide siloxane) – 3c_{40 wt%APPS}



Analytical calculation for $(C_{50.1762} \text{ H}_{54.4486} \text{ O}_{10.72}\text{F}_{2.94}\text{N}_2\text{Si}_{5.2581})_n$ (1060.774 gmol⁻¹)_n: C, 56.81%; H, 5.17%; N, 2.64%; Found: C, 56.95%; H, 5.46%; N, 2.92%.

IR (KBR) (cm⁻¹): 3071(aromatic C-H stretching); 2961(-CH₃ group present in APPS); 1774 and 1717 (asymmetric and symmetric –CO- stretching); 1601 (C=C ring stretching); 1504 (band due to C-F stretching); 1382 (asymmetric C-O-C stretching); 1085, 1022 (Si-O-Si stretching); 801 (Si-C stretching).

6B.4.4 Poly (imide siloxane) – 3d_{40 wt%APPS}



Analytical calculation for $(C_{49.1762}H_{54.4486}O_{10.7281}F_{2.94}N_2Si_{5.2581})_n$ (1048.763 gmol⁻¹)_n: C, 56.32%; H, 5.23%; N, 2.67%; Found: C, 56.81%; H, 2.72%; N, 2.98%.

IR (KBR) (cm⁻¹): 3071(aromatic C-H stretching); 2961(-CH₃ group present in APPS); 1775 and 1723 (asymmetric and symmetric –CO- stretching); 1610 (C=C ring stretching); 1506 (band due to C-F stretching); 1389 (asymmetric C-O-C stretching) ; 1080, 1015 (Si-O-Si stretching); 802 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 8.05-7.13(17.12H), 3.71(s, 1.86H, -CH₂-N<), 1.68-1.58(m, 2.04H, -CH₂-), 0.90-0.55(m, 2.36H, -CH₂-Si), 0.18-0.04(m, 30.91H, Si-CH₃).

6B.4.5 Poly (imide siloxane) – 3e40 wt%APPS



Analytical calculation for $(C_{62.8382} H_{73.6346} O_{12.4591} F_{2.34} N_2 Si_{6.2891})_n (1277.453 \text{ gmol}^{-1})_n$: C, 59.08%; H, 5.81%; N, 2.19%; Found: C, 59.53%; H, 5.78%; N, 2.43%.

IR (KBR) (cm⁻¹): 3068(aromatic C-H stretching); 2962(-CH₃ group present in APPS); 1777 and 1720 (asymmetric and symmetric –CO- stretching); 1610 (C=C ring stretching); 1499 (band due to C-F stretching); 1392 (asymmetric C-O-C stretching) ; 1079, 1016 (Si-O-Si stretching); 799 (Si-C stretching).

¹H-NMR (CDCl₃): δ (ppm) 7.90-7.00 (15.79H), 3.61 (s, 1.56H, -CH₂-N<), 1.76-1.60 (m, 8.44H, -CH₂-), 0.88-0.53(m, 1.82H, -CH₂-Si), 0.15-0.014 (m, 20.60H, Si-CH₃).

6B.5 Results and discussions

6B.5.1 FTIR spectroscopy

The formation of poly (imide siloxane)s were confirmed by FTIR spectroscopy. FTIR spectra of the polyimide films show absorption bands at about 1780 cm⁻¹ (C=O asymmetric stretching) and 1720 cm⁻¹ (C=O symmetric stretching), corresponding to the imide bands. The strong absorption band at 2961 cm⁻¹ is due to the presence of methyl groups attached to silicon molecules in APPS. The strong absorption bands at 1090, 1020 cm⁻¹ (Si-O-Si stretching) and 800 cm⁻¹ (Si-C) are the characteristic for the siloxane group.

6B.5.2 ¹H- NMR spectroscopy

¹H-NMR spectra of the polymers could not be recorded for polymers 3a_{40 wt% APPS} and 3c_{40 wt% APPS} due to insolubility in common organic solvents. ¹H-NMR spectra of the polymers 3b_{40 wt% APPS}, 3d_{40 wt% APPS} and 3e_{40 wt% APPS} was recorded using CDCl₃ as solvent and did not show any amide or acid protons, indicating full imidization. The siloxane incorporation in the polymers was calculated from the integrated peak areas for magnetically different protons from NMR spectra. Table 6B.1 represents the number of aromatic and aliphatic protons calculated from the structures of poly (imide siloxane)s and that found from integrated peak areas for proton NMR spectra. In each of the respective cases it is observed that the ratio of aliphatic / aromatic protons found from the integrated peak areas was a little less than the calculated values, indicating an actual incorporation of siloxane units of about 37 wt% compared to the 40 wt% attempted. The reasons for the somewhat lower siloxane incorporation have been discussed in detail in Chapter 4.

Table 6B.1: Actual incorporation of siloxane in the poly(imide siloxane)sderived from TFAA from ¹H-NMR spectra

Polymer	C-aro	C-ali	F-aro	F-ali	C-ali/aro	F-ali/aro	A - Silo %
3b _{40wt%} APPS	15.46	41.58	18.58	46.60	2.689	2.507	37.29
3d _{40wt% APPS}	16.78	37.628	17.12	37.17	2.242	2.171	38.72
3e _{40wt%} APPS	22.58	50.614	15.79	32.43	2.241	2.054	36.65

C-aro = Theoretical number of aromatic protons calculated from structure C-ali = Theoretical number of aliphatic protons calculated from structure C (ali/aro) = Theoretical ratio of aromatic/aliphatic protons

F (ali/aro) = Found ratio of aromatic/aliphatic protons calculated from integrated peaks A-silo (%) = [F(ali/aro)/C(ali/aro)x 40] =Actual wt% incorporation of siloxane in the polymer structure.

6B.5.3 Polymer solubility and molecular weight determination of the polymers

The solubility of the resulting poly (imide siloxane)s was investigated in different organic solvents. The solubility behavior of the polymers in different solvents is presented in Table 6B.2. The polymers 3b_{40 wt% APPS}, 3d_{40 wt% APPS} and 3e_{40 wt% APPS} exhibited very good solubility in common organic solvents such as chloroform (CHCl₃), dichloromethane (CH₂Cl₂), dimethylformamide (DMF), N, N-dimethyl acetamide (DMAc), and N-methyl-2-pyrrolidinone (NMP). It is interesting to note that the polymers 3a_{40 wt% APPS} and 3c_{40 wt% APPS} were insoluble in any of the common organic solvents despite the incorporation of flexible siloxane units in the polymer backbone, whereas the corresponding homopolyimide 3a was soluble in NMP on heating and 3c was observed to be soluble in many common organic solvents as reported in Chapter 6A. In case of 3a₄₀ wt% APPS and 3c_{40 wt% APPS} the polymerization was done through thermal imidization route. In thermal imidization. Possibly during this heat treatment the weak imido propyl linkages in these polymers may cleave and can lead to unwanted side reaction which in turn leads to insolubility. This also suggests that thermal imidization is not a preferred route of synthesis for these types of polymers.

Polymer	M _w g/mol	PDI	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	Acetone
3a _{40wt%}	-	-	-	-	-	-	-		
3b _{40wt%} Apps	41200	2.5	++	++	++	-	++	++	<u> </u>
3c _{40wt%}	-	-	-	-	-	-	-	-	-
APPS	38600	2.3	++	+	+	-	++	+-+	-
3e _{40wt%}	57900	2.9	++	++	++	-	++	++	-

Table 6B.2: Solubility, molecular weight and PDI of $(3a - 3e)_{40 \text{ wt\% APPS}}$

⁺⁺ soluble at room temperature 30 0 C; + soluble on heating; - insoluble at reflux; M_{w} = weight average molecular weight by GPC; PDI = polydispersity Index.

In comparison to the previous reported homopolyimides 3b, 3d and 3e the corresponding siloxane containing copolymers $3b_{40 \text{ wt\% APPS}}$, $3d_{40 \text{ wt\% APPS}}$ and $3e_{40 \text{ wt\% APPS}}$ exhibited dramatic improvement in solubility as they were observed to be soluble at room temperature in common organic solvents. This improvement in solubility can be

explained because of the combined effect of fluorine in the form of trifluoromethyl groups which tends to increase the fractional free volume and the siloxane moiety incorporated in the polyimide backbone which increases the chain flexibility contributing to the ease of penetration of the solvent molecules in between polymer chains. The solution viscosities of the poly(imide siloxane)s are observed to be greater than 0.35 dL / g and also the GPC molecular weights of these polymers indicates formation of high molar mass products.

6B.5.4 Glass transition temperature versus polymer structure

The poly (imide siloxane)s exhibited no crystallization or melting transition in DSC measurements. These polymers showed however glass transition temperatures which indicate an amorphous or glassy morphology. The glass transition temperature values are summarized in Table 6B.3. In general, lower Tg's are observed for these siloxane containing polyimides compared to the homopolymer analogues. This is due to the presence of the flexible siloxane units in the polymer backbone which increase the chain mobility. The lowest glass transition temperature is observed for poly(imide siloxane) 3e40 wt% APPS synthesized from BPADA, containing two flexible ether linkages. However, the glass transition temperature of 3e40 wt% APPS is significantly higher than that of analogous poly(imide siloxane)s synthesized from 4,4'-bis(p-aminophenoxy-3,3"trifluoromethyl)terphenyl, 4,4'-bis(3"-trifluoromethyl-p-aminobiphenyl ether)biphenyl, and 2.5-bis (3'-2,6-bis(3'-trifluoromethyl-*p*-aminobiphenyl ether)pyridine trifluoromethyl-p-aminobiphenylether)thiopene and BPADA, as reported in Chapter 5B. This is due to the bulky anthracene moiety in the polymer backbone. Glass transition temperatures were not observed for the polymers 3a40 wt% APPS and 3c40 wt% APPS synthesized by the thermal imidization route, which may be due to high chain entanglement or the occurrence of side reactions during the imidization leading eventually to crosslinking and as a manifestation, results in insolubility.

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Table 6B.3: Thermal properties of $(3a - 3e)_{40 \text{ wt\% APPS}}$

Polymer	Ar	DSC T _g (°C)	DMA (tan ∂) T _g (°C)	T _d (°C) in N ₂	Residual mass at 800 °C
3a40wt% APPS	XX	- -	-	463	32.14
3b _{40wt%} APPS	F3C CF3	177	192	442	31.10
3c _{40wt} % APPS	joiot	-	-	441	32.77
3d _{40wt%} APPS)O° O(159	178	434	38.28
3e _{40wt%} APPS		112	145	421	38.63

 $T_d = 5\%$ Weight loss temperature

6B.5.5 DMA measurements

The T_g's taken from the tan ∂ peaks at 10 Hz are given in Table 6B.3. The polymer films showed good storage modulus around 1000 MPa at 40 °C. The tan ∂ values show a maximum at a particular temperature, which indicates the T_g of the polymers. These values are in good agreement with the T_g values indicated by DSC plots. DMA plots of the polymers films 3b_{40wt% APPS}, 3d_{40wt% APPS} and 3e_{40wt% APPS} are shown in Figure 6B.1. DMA of 3a_{40wt% APPS} and 3c_{40wt% APPS} could not be recorded because of the brittle nature of the films.



Figure 6B.1: DMA plots of the poly(imide siloxane)s from anthracene moiety

6B.5.6 Thermal stability

The thermal properties of the copolymers were evaluated by TGA. The TGA thermograms of the polymers are shown in Figure 6B.2 and the thermal properties of the polymers are summarized in Table 6B.3. The 5% weight loss of these polymers are in the temperature range of 421 - 463 °C while 50% weight loss are observed in the temperature range above 500 °C. This indicates good thermal stability of the poly(imide siloxane)s but lower compared to the analogous homo-polyimides. This lowering of the thermal stability of these polymers compared to the respective homopolymers is due to the presence of weak aminopropyl silane linkers in the polymer chain. All these polymers showed high char residues of more than 30 wt% at 800 °C under nitrogen atmosphere.



Figure 6B.2: TGA thermograms of the (3a - 3e)40 wt% APPS

6B.5.7 Mechanical properties

The mechanical properties of thin poly (imide siloxane) films are shown in Table 6B.4. In general, the mechanical properties of the poly (imide siloxane) films are excellent. The poly (imide siloxane) $3e_{40wt\% APPS}$ exhibited the highest elongation at break of up to 110% (Figure 6B.3). This is due to the incorporation of flexible siloxane units in the polymer backbone. It is also observed from Table 6B.4 that the polymer $3e_{40wt\% APPS}$ having two ether linkages show higher flexibility compared to the polymer $3d_{40wt\% APPS}$ containing only one ether linkage per unit. The polymers $3b_{40wt\% APPS}$ and $3c_{40wt\% APPS}$ having bulky and rigid units in the backbone have a lower elongation at break. It is also worth mentioning that the analogous homo-polymers have lower elongation at break values but show higher tensile strength at break and modulus. It was not possible to record mechanical properties of polymer $3a_{40wt\% APPS}$ due to the brittle nature of the film.



Figure 6B.3: Stress -strain plots of the poly(imide siloxane)s (3b - 3e)40 wt% APPS

6B.5.8 Water absorption and dielectric study

Water absorption is an important parameter for materials to be used in electronic applications. Water absorption studies of the poly(imide siloxane)s were done by immersing rectangular pieces of samples (30x10 mm) in double distilled water at 30 °C after taking the initial weight. Final weight was taken after 24 h and the percent water absorption was calculated. A negligible small water uptake was found for these polymers due to the contribution both, of fluorine and siloxane sequences [5] into the backbone of the polyimide. These structural features lead also to low dielectric constant values for these films.

Polymer	Tensile strength (MPa)	Elongation at break (%)	Young's Modulus (GPa)	Water absorption (%) after 24 h	Dielectric constant at 1MHz
3a40wt% APPS	-	-	-	0.08	2.85
3b _{40wt%} APPS	29	73	0.61	0.04	2.63
3c _{40wt%} APPS	31	12	0.63	0.06	2.82
3d 40wt% APPS	27	83	0.58	0.07	2.72
3e _{40wt} % APPS	25	110	0.52	0.11	2.73

Table 6B.4: Mechanical, water absorption and dielectric behavior of $(3a - 3e)_{40 \text{ wt\% APPS}}$

6B.6 Conclusion

Several new co-poly(imide siloxane)s containing anthracene moieties in the main chain have been prepared. In each case the siloxane loading was attempted to 40 wt%. NMR investigation revealed an achieved siloxane incorporation of about 37 wt%. The somewhat reduced value compared to the feed ratio may be in the range of instrument error or some disproportionation reaction of the siloxane chain occurred as reported earlier. The synthesized polymers showed very high flexibility in comparison to the analogous homo-polyimides with an elongation at break upto 110% but at the cost of tensile strength at break and initial modulus values. The flexible siloxane unit reduces the glass transition temperature and affects the thermal stability of the polymers to some extent compared to the respective homopolyimides. However, the thermal and mechanical properties of the polymers are still in the range that these polymers may find application in high temperature cabling application. Beside, these polymers showed very low water absorption (0.04 wt%) and low dielectric constant (2.63) that are essential for electronic applications.

6B.7 References

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Polyimides are high performance materials and are finding a wide range of applications in aerospace, microelectronics and elsewhere. Several potential applications of polyimides have appeared in the literature for advanced technologies such as internal dielectric photo resists, membranes, photoconductors, light emitting diodes and nonlinear optical materials. Many desirable properties of polyimides, including good thermooxidative stability and excellent mechanical properties, contribute to their success. However, aromatic polyimides are generally difficult to fabricate into fibers and films because of their high melting or softening temperatures and insoluble nature in most organic solvents. Current and prior attempts to solubilize and process aromatic polyimides have been made through the synthetic modification of the basic rigid chain structures by the introduction of flexibilizing linkages or molecular asymmetry into the backbone or the addition of bulky or flexible side groups.

Innovative research in the field of fluorinated polymers is ever on an increase. The introduction of fluorine into the polyimides can affect many properties which includes high thermal stability, low moisture absorption, high optical transparencies, and low dielectric constant.

Fluorine in the form of trifluoromethyl group in the polymer backbone is introduced in the polymer structure with the following objectives such as to increase the fractional free volume, decrease moisture uptake and decrease dielectric constant.

On the other hand, incorporation of flexible siloxane segment in the polyimide backbone increase the solubility, processability, impart low moisture uptake, low dielectric constant, thermo-oxidative resistance, low surface energy, and good adhesion properties to the substrate. Poly(imide siloxane)s are thermoplastic segmented copolymers containing a siloxane segment along the backbone chain of the polyimide, it is expected that these copolymers maintain some of the excellent properties of the polyimide such as high temperature stability and mechanical strength and some of the desirable properties of the siloxane such as ductility, adhesion and low moisture permeability as well as low water solubility.

In view of academic and commercial interest we incorporated both trifluoromethyl groups as well as siloxane segment in the polyimides. The following objectives are set for the present thesis:

- Increase the solubility and melt processability of the polyimide
- Reduction of water uptake by the polymer films
- Reduction of modulus without affecting glass transition temperature to great extent
- Reduction of dielectric constant

To fulfill the objectives the following work has been done:

- 1. Synthesis of novel fluorinated poly(imide siloxane)s by incorporation of polydimethylsiloxane segment and pendent –CF₃ group in the polyimide backbone.
- 2. Perform a comprehensive characterization of the fluorinated poly(imide siloxane)s namely structural analysis by elemental analysis, FTIR and NMR techniques, thermal properties by DSC/DMTA and TGA, mechanical properties, water absorption and dielectric properties.
- 3. Comparison of the properties of novel fluorinated poly(imide siloxane)s.

The work has been presented in six chapters.

Chapter 1 of the present thesis gives general introduction and describes in brief the review on poly(imide siloxane)s. The synthesis of the poly(imide siloxane)s by various synthetic routes, their properties and applications in various fields have been described. The role of fluorine on the polyimides has also been discussed. From the literature survey it is clear that;

- 1. Processability can be increased while hydrophilicity and dielectric constant of the polymer can be decreased by incorporation of flexible siloxane linkage in the polymer backbone.
- 2. Fluorine in the form of trifluoromethyl groups in the polymer structure leads to an increase in the fractional free volume and hydrophobic nature of the polymer and decrease the dielectric constant.

Finally the objective and scope of the present investigation have been stated.

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Chapter 2 describes the experimental procedures for purification of chemicals and materials used for synthesis of monomers and polymers and various analytical methods for characterization and testing of monomers and polymers.

Chapter 3 deals with the synthesis of already reported diamines for the purpose of ease of discussion related to the new polyimides prepared from them. A new monomer 9, 10bis (3"-trifluoromethyl-*p*-aminobiphenyl ether)anthracene (TFAA). has been synthesized by reaction by the reaction of 9,10- bis (2-fluoro benzotrifluoride) anthracene with 4amino phenol. The reaction was carried out in NMP as solvent in the presence of excess of potassium carbonate as base. Toluene was used to remove the water formed in the acid-base reaction between phenol and base. The monomer was characterized by elemental analysis, melting point, Fourier Transform Infrared Spectroscopy(FTIR) and Nuclear Magnetic Resonance(NMR) spectroscopy. IR spectra of the monomer show peaks at 3420, 3345cm⁻¹ for (-NH₂). In ¹H-NMR, the- NH₂ peak was observed in 5 - 5.5 ppm and aromatic protons at 7.79- 6.69 ppm. In ¹³C-NMR spectra the carbon attached with – CF₃ group showed quartet of coupling constant 271.5 Hz due to C-F coupling.

Chapter 4 deals with the synthesis of four new poly(imide siloxane)s using dianhydride system as ODPA with different diamines 4,4'-bis(p-aminophenoxy- 3,3"-trifluoromethyl) 4,4'-bis(3''-trifluoromethyl-*p*-aminobiphenyl ether)biphenyl, 2.6-bis(3'terphenyl, trifluoromethyl-p-aminobiphenyl ether)pyridine and 2,5-bis (3'-trifluoromethyl-paminobiphenylether)thiopene respectively each with 40 wt% of amino-propyl terminated polydimethylsiloxane (APPS) as a co-monomer. The solution imidization technique using ODCB was very much successful in synthesizing the poly(imide siloxane)s. The polymers were well characterized by FTIR and NMR techniques. The thermal, mechanical, water sorption, and dielectric properties of these polymers were studied. Both proton and silicon NMR indicated the siloxane loading was about 36% although it was attempted to 40 wt%. The synthesized polymers exhibited very good solubility at room temperature (30 °C) in common organic solvents compared to the previously reported analogous homopolyimides without siloxane. The glass transition temperature of the poly(imide siloxane)s were in the range of 160 - 225 °C. The glass transition temperature of 1b containing rigid quadriphenyl unit in the polmer backbone was highest (225 °C) in the series and are comparable with the commercially available Ultem [®] 1000 (Tg, 217 °C). These poly(imide siloxane)s showed good thermal stability in nitrogen at 5% weight loss occurred above 430 °C. Films of these poly (imide siloxane)s exhibited tensile strength upto 30 MPa and high elongation at break upto 103% depending upon the structure of the repeating unit. The films of these polymers showed negligibly low water uptake in the range of 0.02 - 0.07% and low dielectric constant of 2.36 - 2.52 at 1 MHz.

Chapter 5A reports successful synthesis of four new poly(ether imide)s on reaction with bisphenol-A (diphthalic anhydride) with different trifluoromethyl-substituted diamines 4'-bis(*p*-aminophenoxy-3''-trifluoromethyl)terphenyl, 4,4'-bis(3"-trifluoromethyl-paminobiphenylether)biphenyl, 2,6-bis(3'-trifluoromethyl-p-aminobiphenyl ether)pyridine and 2,5-bis (3'-trifluoromethyl-p-aminobiphenylether)thiopene respectively by thermal imidization technique. The polymers were well characterized by spectroscopy, thermal, mechanical and dielectric properties. The synthesized polymers exhibited excellent solubility at room temperature (30 °C) in different organic solvents. The resulting poly(ether imide)s showed high thermal stability for 5% weight loss temperature of 504 -522° C in nitrogen and 470 - 489 °C in air. Thiophene moiety containing poly(ether imide) showed minimum thermal stability in air compared to the other polymers. This could be attributed because of loss of aromaticity due to oxidation of thiophene. These polymers showed good mechanical strength of 69 -97 MPa, a modulus of elasticity up to 1.56 GPa and elongation at break up to 20%. These poly(ether imide)s were observed to have low moisture uptake of 0.19 - 0.30% and low dielectric constant of 2.79 - 3.1 at 1 MHz.

Chapter 5B deals with the synthesis of poly(imide siloxane)s in the previously reported homopolymers discussed in chapter 5A. Total eight new poly(imide siloxane)s have been prepared and the properties of the resulting polymers were investigated thoroughly; and compared with the analogous homopolymers. The polymers showed low T_g 's depending on siloxane incorporation compared to the homopolymers reported in Chapter 5A and poly(imide siloxane)s reported in Chapter 4. The resulting poly(imide siloxane)s showed good thermal stability of ~ 450 °C in nitrogen and showed moderate thermal stability of 400 °C in air. The thermal stability values of the poly(imide siloxane)s in nitrogen atmosphere are comparable with the thermal stability of poly(imide siloxane)s synthesized from ODPA in Chapter 4. The polymers showed low tensile strength but high elongation at break in the range of 63 – 144% with 40 wt% siloxane loading and 18 – 37% with 20 wt% siloxane loading compared to the homopolymers reported in Chapter 5A. The poly(imide siloxane)s with quadriphenyl unit in the polymer backbone synthesized from BPADA with 40 wt% siloxane loading showed higher elongation at break compared to the quadriphenyl containing unit in the polymer backbone synthesized from ODPA. The polymer films absorbed negligibly small amount of water 0.02 - 0.08% for poly(imide siloxane)s with 40 wt% siloxane loading and 0.11-0.20% for poly(imide siloxane)s with 40 wt% siloxane loading. The properties of the poly(imide siloxane)s with 40 wt% loading synthesized from ODPA. The dielectric constant reported is as low as 2.39 for poly(imide siloxane)s with 40 wt% siloxane loading.

Chapter 5C deals with the variation of properties observed by varying the siloxane loading by using the same dianhydride; bisphenol-A-di(phthalic anhydride) and with the fluorinated diamine namely 4, 4'-bis (3"-trifluoromethyl-*p*-aminobiphenyl ether)biphenyl with varying weight percentages of amino-propyl terminated polydimethylsiloxane (APPS) from 5-40 wt%. The properties are compared with the respective homopolymer 2b discussed in Chapter 5A. The polymers showed glass transition temperatures 203 – 107 °C, thermal stabilities 452 – 418 °C, tensile strength 75 – 24 MPa, water uptake 0.19 - 0.02 and dielectric constant 2.76 - 2.43 which decreased sequentially increase in siloxane loading.

Chapter 5D reports preparation of perfectly block copolymers of varying soft and hard block lengths and detailed investigation of their properties by NMR, DSC, DMA analysis and mechanical properties. DSC and DMA revealed increase in glass transition temperatures with increase in the soft and hard block lengths. The block copolymer showed higher T_g compared to the randomly segmented copolymer reported in Chapter 5B. At very higher block lengths the synthesized block copolymer showed T_g comparable with the T_g value of the homopolymer reported in Chapter 5A.

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Chapter 6A reports synthesis and characterization of novel poly(ether imide)s with five commercially available dianhydrides namely pyromellitic dianhydride (PMDA), 4,4'- (Hexafluoro-isopropylidene)diphthalic anhydride (6FDA), 3, 3', 4, 4'-Benzophenone tetracarboxylic dianhydride (BTDA), o-diphthalic anhydride (ODPA), bisphenol-A-di(phthalic anhydride) (BPADA) with the new diamine monomer TFAA. The resulting poly(ether imide)s exhibited high thermal stability of greater than 500 °C, good mechanical strength upto 80 MPa and Young's modulus upto 3.2 GPa. The polymers showed band gap energy values 2.06 - 2.58 eV that lies in the visible range of the electromagnetic spectrum. High glass transition temperature and thermal stability was observed in case of PMDA containing poly(ether imide). All the poly(ether imide)s showed char residues greater than 60% which indicates good thermal stability.

Chapter 6B reports synthesis and characterization poly(imide siloxane)s incorporated with 40 wt% siloxane using TFAA and APPS as diamines and different commercially available dianhydrides. The resulting poly(imide siloxane) copolymers exhibited good thermal stability in the range of 421 - 463 °C however lower than the respective homopolyimides. The polymers showed low tensile strength but high elongation at break upto 110% in comparison to the homopolyimides reported in Chapter 6A. The polymer films absorbed negligibly small amount of water as low as 0.04% and showed low values dielectric constant.

Conclusions

The principal goal of this research was to develop new poly(imide siloxane)s. In this regard four poly(imide siloxane)s have been synthesized from ODPA; eight poly(imide siloxane)s have been synthesized from BPADA by varying the siloxane loading together with the respective homopolymers synthesized from BPADA. Tailoring of properties has been observed by synthesizing eight poly(imide siloxane)s from BPADA by varying the siloxane loading to various weight percentages. All the poly(imide siloxane)s were synthesized following the solution imidization route. Five new poly(ether imide)s were developed from a new anthracene moiety containing diamine monomer with five different dianhydrides PMDA, 6FDA, ODPA, BPADA and BTDA. The work was further extended and poly(imide siloxane)s was prepared with the

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same anthracene moiety containing monomer and with the same dianhydrides with 40 wt% siloxane loading.

The synthesized new poly(ether imide)s, copoly(imide siloxane)s and diamine monomer was well characterized by elemental analysis, IR and NMR techniques. The significant findings are as follows:

- 1. Poly(imide siloxane)s synthesized from ODPA and BPADA, showed excellent soluble properties in common organic solvents such as NMP, THF, DMF, DCM CHCl₃ and DMAc at room temperature. The exceptionally high solubility of the poly(imide siloxane)s is due to the presence of flexible amino-propyl linkages in the polymer backbone which imparts ease of penetration of solvent molecules in between the polymer chains and bulky -CF₃ groups which reduce the chain packing density and hence enhance the solubility to a great extent.
- 2. Thermal stability shows a decrease for the siloxane containing polymers compared to the respective homopolymers because of the weak aminopropyl linkages present in the polymer backbone. However, thermal stability is not in any case less than 400 °C even when thermal stability was studied in air which indicates good thermal stability.
- 3. Incorporation of both fluorine as well as siloxane units in the polymer backbone reduces the water uptake drastically leading the poly(imide siloxane)s films to be hydrophobic in nature. The siloxane unit [-Si-O-Si] being inert in nature together with its low surface energy of ~21mJ / cm² leads to dramatic reduction in water uptake values. About 10 times lowering of water uptake values were observed in case of poly(imide siloxane)s containing 40 wt% siloxane loading compared to the respective homopolymers and thermal, mechanical, dielectric properties and water absorption of these polymers have been evaluated. Water uptake value as low as 0.02% has been reported in the entire study.
- 4. The poly(ether imide)s synthesized from the novel diamine monomer containing anthracene moiety showed high glass transition temperatures and high thermal stabilities with light emitting properties. The poly(imide siloxane)s synthesized however showed lower glass transition temperature and good thermal stability with low values of dielectric constant.

5. Reduction in dielectric constant is observed in case of poly(imide siloxane)s compared to the respective poly(ether imide)s due to the incorporation of both fluorine as well as siloxane sequences present in the polymer backbone. Dielectric constant value as low as 2.36 with 40 wt% siloxane loading has been found in the entire investigation.