

Synthesis, Characterization, and Comparison of Properties of Novel Fluorinated Poly(imide siloxane) Copolymers

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ABSTRACT: Four new poly(imide siloxane) copolymers were prepared by a one-pot solution imidization method at a reaction temperature of 180°C in *ortho*-dichlorobenzene as a solvent. The polymers were made through the reaction of *o*-diphthaleic anhydride with four different diamines—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, and 2,5-bis(3'-trifluoromethyl-*p*-aminobiphenylether)thiopene—and aminopropyl-terminated poly-dimethylsiloxane as a comonomer. The polymers were named **1a**, **1b**, **1c**, and **1d**, respectively. The synthesized polymers showed good solubility in different organic solvents. The resulting polymers were well characterized with gel permeation chromatography, IR, and NMR techniques. ¹H-NMR indicated that the siloxane loading was about 36%, although 40 wt % was attempted. ²⁹Si-NMR confirmed that the low siloxane incor-

poration was due to a disproportionation reaction of the siloxane chain that resulted in a lowering of the siloxane block length. The films of these polymers showed low water absorption of 0.02% and a low dielectric constant of 2.38 at 1 MHz. These polyimides showed good thermal stability with decomposition temperatures (5% weight loss) up to 460°C in nitrogen. Transparent, thin films of these poly(imide siloxane)s exhibited tensile strengths up to 30 MPa and elongations at break up to 103%, which depended on the structure of the repeating unit. The rheological properties showed ease of processability for these polymers with no change in the melt viscosity with the temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1831–1841, 2008

Key words: dielectric properties; mechanical properties; polyimides; rheology; thermal properties

INTRODUCTION

Polyimides are known for their excellent thermal stability in air, chemical resistance, and mechanical and electrical properties^{1–12} and have been considered for various applications, such as high-performance aerospace materials and gas-separation membranes.¹³ Polyimides are receiving increased attention for interlayer dielectrics^{4,6,14} because of their low dielectric constant, low water absorption capacity, low refractive index, and low coefficient of thermal expansion. Despite such attractive properties, this class of polymers suffer from insolubility and intractability, which cause difficulties in both synthesis and processing. Therefore, the processing of the polyimides is carried out with soluble poly(amic acid) precursors, which are cast onto glass plates and converted to thin polyimide films by a rigorous thermal treatment. This process has been observed to have certain limitations, including the emission of volatile byproducts during curing and the storage instability of the poly(amic acid) intermediate.¹⁵ Therefore, much effort has been spent on synthesizing tractable,

processable polyimides that maintain reasonably high strength and environmental stability. Solubilization of the polyimides has been targeted by several means, such as the introduction of flexible linkages, bulky substituents, and bulky units within the polymer backbone, noncoplanar monomers, or alicyclic monomers and the incorporation of pendent –CF₃ groups.^{16–21} The main goal of all such approaches is the reduction of polymer chain–chain interactions, reduction of chain packing and charge-transfer electronic polarization interactions. In this respect, the incorporation of the flexible siloxane segment into the polyimide backbone imparts enhanced solubility, reduced water sorption, increased gas permeability, good thermal and ultraviolet stability, resistance to degradation in aggressive oxygen environments, impact resistance, and modified surface properties.^{22–26} These interesting properties make poly-siloxane-modified polyimides useful materials for aerospace applications and electronic devices. In addition to enhanced solubility and processability, another goal of polyimide research is to obtain reduced dielectric-constant behavior. In addition to controlling the glass-transition temperature (*T*_g) and processability, polyimides modified with siloxane segments have excellent interfacial adhesion at the polyimide–substrate interface.^{27–31} The first poly(imide siloxane) to be reported³² was prepared

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from pyromellitic dianhydride with numerous low-molecular-weight amine-terminated siloxane dimers. Summers²⁶ synthesized poly(imide siloxane)s with various weight percentages of amine-terminated polydimethylsiloxane (e.g., 5, 10, 20, and 40 wt %) and different molecular weights (number-average molecular weight = 900–10,000 g/mol) into a polyimide based on 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 3,3'-diaminodiphenylsulfone, which provided desired improvements in the bulk and surface properties. Sumitomo Bakelite Co., Ltd., prepared, as adhesive tape, polyimides modified by aminopropyl-terminated polydimethylsiloxane (APPS) under the trade name SIM.²⁷ All studies conducted so far that have been related to poly(imide siloxane) have focused on the content and molecular weight of the siloxane segment and properties thereby affected, such as the mechanical, electrical, and thermal properties and surface morphology, because of the incorporation of the siloxane segment and the existence of microphase separation in the poly(imide siloxane) by thermal analysis and electron microscopy.³³

In our previous work,^{16–20,34} we found that the incorporation of pendent $-\text{CF}_3$ groups into the polymer backbone enhanced the polymer solubility to some extent in organic solvents. However, the solution imidization was not very successful as the polymer came out from the polymerizing solvent. In this work, a dianhydride [*o*-diphthaleic anhydride (ODPA)] and a series of fluorinated diamines coupled with 40 wt % APPS were systematically chosen for the synthesis of poly(imide siloxane)-segmented copolymers. The polymers were prepared by the one-pot solution synthesis of the reactants in *ortho*-dichlorobenzene (ODCB). Structure–property relationships, solubility characteristics, thermal properties, spectroscopy, rheology, scanning electron microscopy (SEM), and dielectric behavior are reported in this article.

EXPERIMENTAL

General consideration

Carbon, hydrogen, and nitrogen of the compounds were analyzed by the pyrolysis method. ¹H-NMR, ¹³C-NMR, and ²⁹Si-NMR were recorded on a Bruker (Switzerland) 300-MHz instrument with CDCl_3 as a solvent. IR spectra of the polymer films were recorded with a Netzsch (Germany) 870 Fourier transform infrared (FTIR) spectrophotometer. Differential scanning calorimetry (DSC) measurements were made on a Netzsch DSC 200PC instrument at a heating/cooling rate of 20°C/min under nitrogen. T_g was taken at the middle of the step transition in the second heating run. The thermal decomposition

behavior of these polymers was measured on a Netzsch TG 209 F1 thermogravimetric analyzer at a heating rate of 10°C/min under nitrogen. Dynamic mechanical thermal analysis was performed on a TA Instrument (New Castle, DE) DMA-2980 under tension mode on thin-film samples at a heating rate of 10°C/min and was run at a frequency of 1 Hz. Mechanical properties such as the tensile strength and elongation at break of the thin polymer films (40 × 0.1 mm) were determined by elongation at room temperature on a Hounsfield (UK) H10KS-0547 instrument under a strain rate of 5%/min for the sample (grip) length. Gel permeation chromatography was measured with a Waters (Milford, MA) 2414 refractive-index detector at 1 mL/min (flow rate) and was run in the solvent tetrahydrofuran (THF). Dry specimens were made by the samples being kept at 80°C overnight under a high vacuum, and the water absorption of the films was measured with a Sartorius (Switzerland) balance with a sensitivity of 10⁻⁶ g. The dry films were immersed into double-distilled water for 72 h at 30°C. The rheology behavior of the films was studied with an AR-1000 rheometer. X-ray diffraction was studied with a PW-1710 (Philips, Holland) X-ray diffractometer with Cu K α targets at 2 mm at a scanning rate of 0.05° 2 θ /s, at a chart speed of 10 mm/2 θ , in a range of 5000 c/s, and at 40 kV and 20 mA to get an idea of the amorphous nature of the films. SEM was used to study the morphology of the materials prepared with a JSM-6360 scanning electron microscope from JEOL Co. (Tokyo, Japan) The dielectric constant of the poly(imide siloxane) films (0.1 mm) was measured with a Hewlett–Packard (Palo Alto, CA) model HP4192A parallel-plate capacitance meter. The diode was fabricated by metallization (Au–Pd) of both surfaces of the films for better contact, and the measurement was performed at multiple frequencies and at different temperatures.

Starting materials

All reagents were purchased from Aldrich (United States) and Gelest, Inc. (United States), and used as received unless otherwise noted. ODPAs (97%; Aldrich) was heated at 120°C overnight before use. APPS ($n = 8.31$) was purchased from Gelest. ODCB (E. Merck, India) was used as received. Methanol was purchased from Ranbaxy Fine Chemical, Ltd. (India). The diamine monomers used in this investigation were prepared with the procedure reported in our previous articles.^{16,17,34}

Polymerization

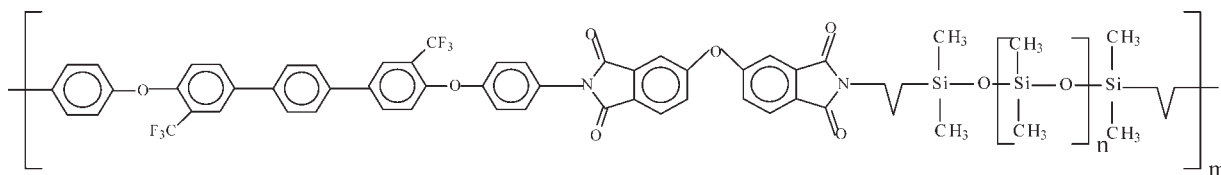
The polymerization reactions were conducted through the reaction of ODPAs and two different di-

amines in a random fashion. The reactions were conducted under a constant flow of nitrogen. A representative polymerization procedure can be described as follows.

A 50-mL, three-necked, round-bottom flask equipped with a nitrogen inlet, magnetic stirrer, and Dean-Stark trap fitted with a condenser was charged with 0.605 g (1.95 mmol) of ODP, 0.59 g (1.024 mmol) of 4,4'-bis(*p*-aminophenoxy-3,3''-trifluoromethyl)terphenyl, and 0.80 g (0.926 mmol) of APPS, and 20 mL of 1,2-dichlorobenzene was 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 polymeric solution was then cooled to room temperature and was precipitated from methanol. The resulting precipitate was then collected by filtration and placed in an oven maintained at a temperature of 120°C for 5 h to remove all traces of the solvent. The measured amount of the polymer was then solubilized in dichloromethane (CH₂Cl₂), and the film was then cast onto a Petri dish and heated in a vacuum oven at 80°C overnight. Transparent, pale-yellow films were obtained for all four polymers.

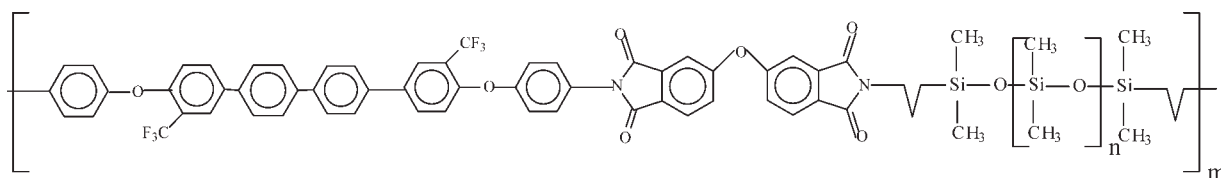
Poly(imide siloxane) 1a



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 band), 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.

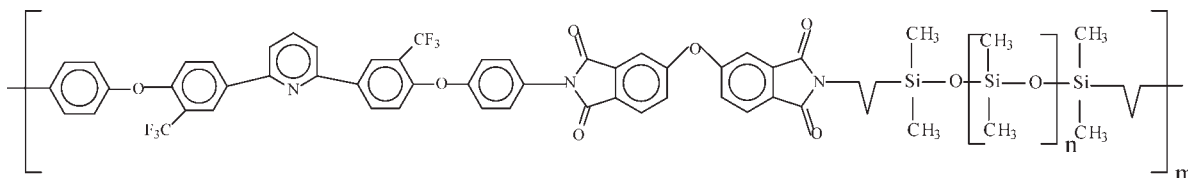
Poly(imide siloxane) 1b



IR (KBr, cm⁻¹): 3477 (—N< stretching), 3069 (aromatic C—H stretching), 2961 (—CH₃ group present in APPS), 1775 and 1720 (asymmetric and symmetric —CO— stretching), 1610 (C=C ring stretching band), 1506 (band due to C—F absorption), 1392 (asymmetric C—O—C stretching). ¹H-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.

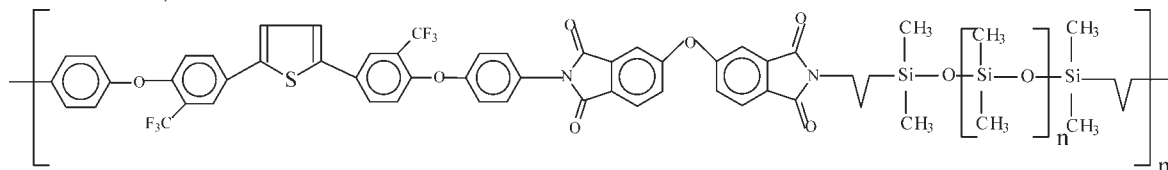
Poly(imide siloxane) 1c



IR (KBr, cm^{-1}): 3478 ($-\text{N}<$ stretching), 3071 (aromatic C—H stretching), 2961 ($-\text{CH}_3$ group present in APPS), 1775 and 1720 (asymmetric and symmetric $-\text{CO}-$ stretching), 1610 (C=C ring stretching band), 1506 (band due to C—F absorption), 1392 (asymmetric C—O—C stretching). $^1\text{H-NMR}$ (CDCl_3 ,

δ , ppm): 8.46–7.17 (15H), 3.74 (s, 4H, $-\text{CH}_2-\text{N}<$), 1.69 (s, 4H, $-\text{CH}_2-$), 0.57 (s, 4H, $-\text{CH}_2-\text{Si}$), 0.26 (m, 60H, Si— CH_3). $^{13}\text{C-NMR}$ (CDCl_3 , 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.

Poly(imide siloxane) **1d**



IR (KBr, cm^{-1}): 3477 ($-\text{N}<$ stretching), 3071 (aromatic C—H stretching), 2961 ($-\text{CH}_3$ group present in APPS), 1776 and 1720 (asymmetric and symmetric $-\text{CO}-$ stretching), 1610 (C=C ring stretching band), 1499 (band due to C—F absorption), 1392 (asymmetric C—O—C stretching). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 8.04–7.07 (14H), 3.66 (s, 4H, $-\text{CH}_2-\text{N}<$), 1.69 (s, 4H, $-\text{CH}_2-$), 0.57 (s, 4H, $-\text{CH}_2-\text{Si}$), 0.27 (m, 60H, Si— CH_3). $^{13}\text{C-NMR}$ (CDCl_3 , 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.

RESULTS AND DISCUSSION

The reaction scheme and polymer structures are shown in Figure 1. The polymers were prepared by a conventional one-pot solution imidization method. A high-boiling nonpolar solvent was preferred; in this synthesis, ODCB was used as a solvent with a

solid content of 20 wt %. The reactants, diamines and dianhydrides, were mixed in a random fashion, the polymerization temperature was raised to 180°C , and the reaction was continued for 6 h. During the course of the reaction, water that formed because of imidization was removed azeotropically by ODCB, and accordingly, fresh solvent was added to make up for the solvent loss. After the completion of 6 h at 180°C , the reaction temperature was brought down to room temperature, and the polymer solution was precipitated into 100 mL of methanol. The fibrous product that was obtained was dried and dissolved in 20 mL of CH_2Cl_2 and was reprecipitated from methanol. The fibrous products that were obtained were dried at 80°C overnight and used for further analysis. The molar masses of the poly(imide siloxane)s reported in Table I indicate the formation of high-molecular-weight products. The polymer solutions (15 wt %) in CH_2Cl_2 were poured into flat-bottom Petri dishes, and the films were prepared

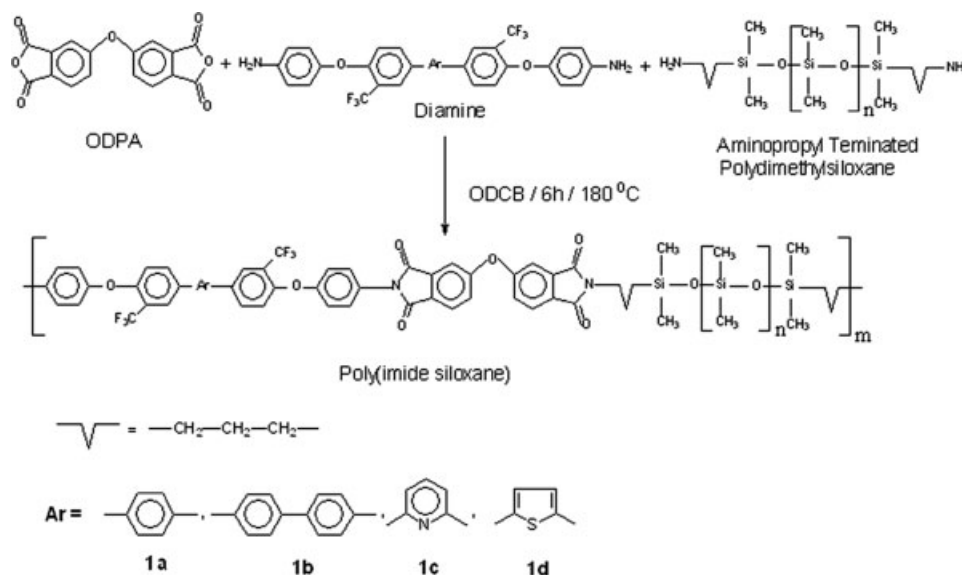


Figure 1 Reaction scheme and structures of poly(imide siloxane).

TABLE I
Number-Average Molecular Weight (M_n) and Polydispersity Index (PDI) Values of the Polymers

Polymer code	Molecular formula ^a	Carbon (%)		Hydrogen (%)		Nitrogen (%)		M_n	PDI
		Calcd	Found	Calcd	Found	Calcd	Found		
1a	C _{45.444} H _{50.533} F _{3.15} O _{10.472} N ₂ Si _{4.897}	55.15	56.26	5.15	4.69	2.83	3.11	24,500	1.85
1b	C _{48.3669} H _{53.67} F _{3.03} O _{10.618} N ₂ Si _{5.103}	56.19	56.56	5.23	4.98	2.71	2.98	32,800	2.32
1c	C _{44.919} H _{50.008} F _{3.15} O _{10.472} N _{2.525} Si _{4.897}	54.48	55.02	5.09	4.64	3.57	3.82	41,100	2.47
1d	C _{44.431} H _{49.541} F _{3.144} O _{10.479} N ₂ Si _{4.897} S _{0.524}	53.71	54.79	5.03	4.65	2.82	2.94	33,800	1.91

^a Based on the feed composition.

by the evaporation of the solvent at a control rate at 30°C overnight. The Petri dishes were kept in a vacuum oven, the temperature of the oven was slowly raised to 120°C, and they were kept under a continuous vacuum for 5–6 h to remove any trace of the solvent.

Polymer solubility

The solubilities of the resulting poly(imide siloxane)s were investigated in different organic solvents. The solubility behavior of the polymers in different solvents is presented in Table II. These polymers exhibited very good solubility behavior in common organic solvents such as chloroform (CHCl₃), CH₂Cl₂, dimethylformamide (DMF), *N,N*-dimethyl acetamide (DMAc), and *N*-methyl-2-pyrrolidinone (NMP). In comparison to the previous polymers reported,¹⁹ these polymers exhibited dramatic improvements in solubility. These improvements in solubility were due to the combined effect of fluorine in the form of trifluoromethyl groups, which tended to increase the fractional free volume, and the siloxane moiety incorporated into the polyimide backbone, which increased the chain flexibility, contributing to the ease of penetration of the solvent between polymer chains.

Spectroscopy

The formation of poly(imide siloxane) was confirmed by FTIR spectroscopy. FTIR spectra of the polyimide films showed absorption bands at about 1780 (C=O asymmetric stretching) and 1730 cm⁻¹ (C=O symmetric stretching) that corresponded to imide bands.

The absorption band at 2961 cm⁻¹ was due to the presence of methyl groups in APPS. No absorption band existed at 3400–2900 cm⁻¹ corresponding to amide (—NH—) and acid (—OH) stretching or at 1660 cm⁻¹ corresponding to amide (C=O) stretching. ¹H-NMR spectra of the polymers also did not show any amide or acid protons, indicating full imidization. The representative ¹H-NMR spectrum of poly(imide siloxane) **1b** is shown in Figure 2. There is very good matching of the integrated peak areas for chemically different protons in all the polymers.

The siloxane incorporation in the polymers was calculated from the integrated peak areas of ¹H-NMR spectra. The gross molecular formula of the copolymers can be derived from the gross composition of the raw materials; for example, for the terphenyl-containing polymer, the molecular formula of the copolymer can be presented as —(APPS)_{0.4950}—(ODPA)₁—(Quadri)_{0.505}—. With this molecular formula for copolymer **1b**, the calculated ratio of the different aromatic protons contributed by ODPA and terphenyl to the total aliphatic protons contributed by APPS is 17.11:36.56. The ¹H-NMR spectrum in Figure 2 shows the corresponding value of 98.84:18.72. Table III presents 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 ¹H-NMR spectra. The different types of protons explained by this calculation are marked in Figure 2. In each of the following cases, it is observed that the ratio of aromatic protons to aliphatic protons found from the integrated peak areas is more than the calculated values from the gross molecular structure.

TABLE II
Solubilities of the Polymers

Polymer	NMP	DMF	DMAc	DMSO	THF	CHCl ₃	CH ₂ Cl ₂	Acetone
1a	+	+	+	—	+	+	+	—
1b	+	+	+	—	+	+	+	—
1c	+	+	+	—	+	+	+	—
1d	++	+	+	—	+	+	+	—

+ = soluble at room temperature (30°C); — = insoluble at reflux.

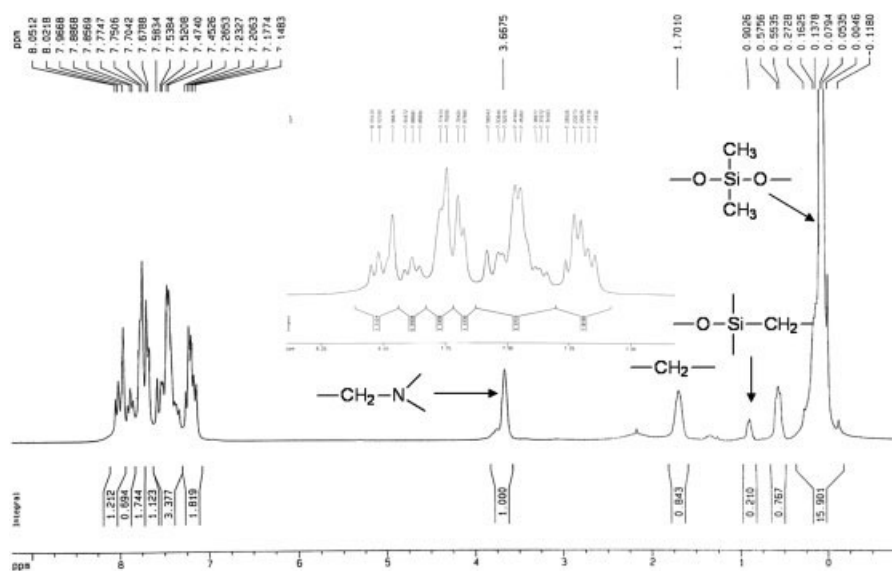


Figure 2 $^1\text{H-NMR}$ spectrum of poly(imide siloxane) **1b**.

Although each of the poly(imide siloxane)s was prepared with the goal of incorporating a 40 wt % siloxane loading, the actual incorporation found was around 36 wt %. Arnold et al.³⁵ tried to incorporate various amounts of siloxane into the polyimide backbone, but the incorporation was found to be less than that attempted, and no proper explanation has yet been given regarding this lessening of incorporation in the polyimide backbone. In another investigation, Pechar et al.³⁶ reported 22 and 41 wt % siloxane incorporation when they attempted 20 and 40 wt % incorporation, respectively.

To get an answer for the anomaly of siloxane incorporation, we recorded $^{29}\text{Si-NMR}$ spectra of these polymers. The representative NMR spectrum of polymer **1b** is shown in Figure 3. For better understanding, the $^{29}\text{Si-NMR}$ spectrum of APPS is also presented in the figure. $^{29}\text{Si-NMR}$ of APPS shows two different silicone peaks at 8 and -28 ppm corresponding to the main chain $-\text{O}-\text{Si}-\text{O}-$ and terminal $-\text{O}-\text{Si}-\text{C}-$ signal connected to allyl amine, showing the integrated peak areas in a ratio

of 8.31 : 2. This in turn tells us that the siloxane block length in APPS is 8.31. In the case of copolymer **1b**, as shown in Figure 3, the main chain $-\text{O}-\text{Si}-\text{O}-$ decreases to 7.5 from 8.31; this indicates a reduction in the siloxane block length during polymerization. This may be due to an amic acid catalyzed equilibration reaction; a plausible mechanistic scenario for this amic acid mediated siloxane equilibration reaction involves intermolecular catalysis by the amic 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 gel permeation chromatography results.

T_g versus the polymer structure

The poly(imide siloxane)s exhibited no crystallization or melting transition in DSC measurements.

TABLE III
Calculated Number of Aromatic and Aliphatic Protons from the Gross Molecular Structure from the Feed Ratio Versus the Protons Found from NMR

Polymer	C-aro	C-ali	F-aro	F-ali	C-aro/ali	F-aro/ali	A-silo (%)
1a	15.45	35.08	37.8	77.69	0.440	0.487	36.208
1b	17.11	36.56	9.84	18.72	0.468	0.526	35.615
1c	14.93	35.08	14.96	31.68	0.425	0.472	36.046
1d	14.38	35.16	12.89	28.21	0.409	0.457	35.808

C-aro = theoretical number of aromatic protons calculated from the structure; C-ali = theoretical number of aliphatic protons calculated from the structure; C-aro/ali = theoretical ratio of aromatic protons to aliphatic protons; F-aro/ali = found ratio of aromatic protons to aliphatic protons calculated from integrated peaks; A-silo (%) = actual weight percentage incorporation of siloxane in the polymer structure.

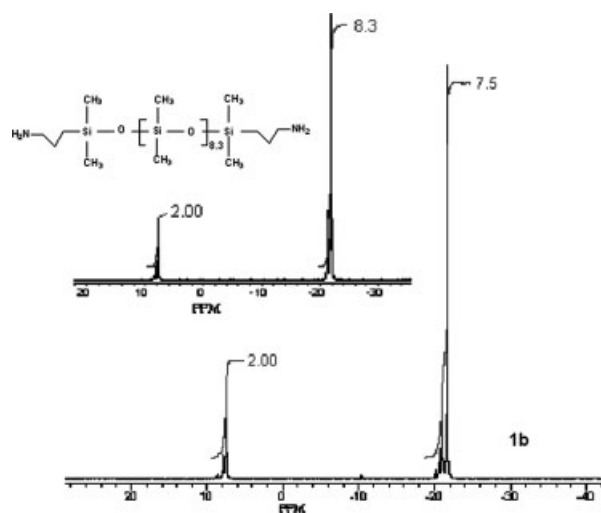


Figure 3 ^{29}Si -NMR spectra of APPS and polymer **1b**.

These polymers showed T_g , which indicated an amorphous or glassy morphology. X-ray diffraction patterns of all four poly(imide siloxane)s also indicated amorphous patterns, which exhibited a broad peak around 14° (2θ). DSC curves of the polymers are shown in Figure 4. The glass-transition values are summarized in Table IV.

Polymer **1b** exhibited the highest T_g values of the polymers, and this was due to the presence of a rigid quadriphenyl unit in the backbone. The next highest glass transition was observed for the polymer containing a terphenyl unit, that is, **1a**, because of the rigid unit in the polymer backbone. The following order of glass transitions was obtained: quadriphenyl > 1,4-diphenyl benzene > 2,6-diphenyl pyridine > 2,5-diphenyl thiophene. This order could be explained on the basis of three factors: rigidity, cate-

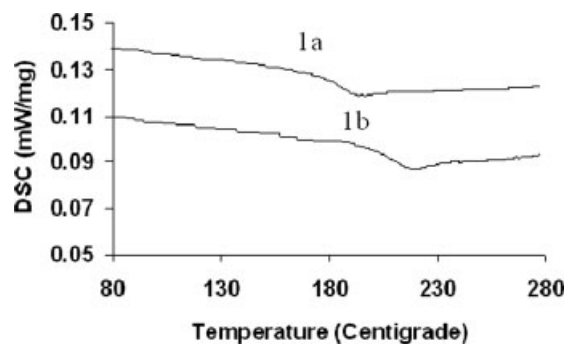


Figure 4 DSC plots of the polymers, **1a** and **1b**.

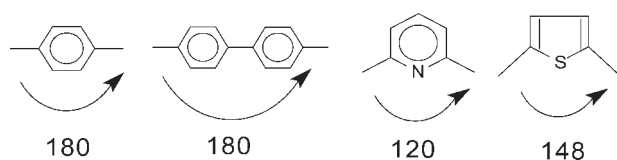
nation angles of different groups, as shown in Scheme 1, and polarity.

A macromolecule exhibits a more extended geometry (i.e., a higher catenation angle provided by different building blocks is expected to lead to a higher T_g). Similarly, if the polymer molecule is built up of rigid units, it is expected to have a higher T_g . The catenation angle between 1,4'-diphenyl benzene and 4,4'-diphenyl biphenyl units is the same, that is, 180° ; however, the polymer containing 4,4' diphenyl biphenyl units exhibited a higher T_g because of the rigidity of this unit. T_g of the polyimides containing pyridine and thiophene units in the polymer backbone showed a different behavior. A lower glass transition was observed for the thiophene-containing polymers than the pyridine-containing polymers, although the catenation angle for the thiophene moiety was 148° which was higher than that of the pyridine moiety, 120° . This may be due to the polarity of the pyridine ring. Pyridine has a more extended geometry than thiophene; at the same time, pyridine has 4 times more polarity than thiophene ($\mu_{\text{pyridine}} = 7.4 \times 10^{-30} \text{ Cm}$, $\mu_{\text{thiophene}} = 1.83 \times 10^{-30} \text{ Cm}$), and

TABLE IV
Thermal Properties of Poly(imide siloxane)

Polymer	Ar	T_g ($^\circ\text{C}$)		T_g ($^\circ\text{C}$) by DMA ($\tan \delta$)	T_d ($^\circ\text{C}$)		Residual mass at 800°C
		DSC ¹⁹	DSC		5% weight loss	50% weight loss	
1a		242	172	205	434	514	32.23
1b		254	225	231	460	547	35.71
1c		241	162	151	438	565	37.49
1d		234	160	141	441	558	36.28

T_d = decomposition temperature.



Scheme 1

this is the probable reason for the higher T_g for pyridine-ring-containing polymers. It can also be observed from Table IV that polymers **1a**, **1b**, **1c**, and **1d** showed T_g 's lower than those of the respective homopolymers.¹⁹ This was due to the incorporation of flexible siloxane units into the polyimide backbone, which weakened the T_g 's to some extent, indirectly indicating good microphase separation. It is also to be noted that T_g of **1b** was higher than that of commercially available Ultem 1000 ($T_g = 217^\circ\text{C}$) based on bisphenol A diphthaleic anhydride.

Thermal stability

The thermal properties of the copolymers were evaluated by thermogravimetric analysis (TGA). The TGA thermograms of the polymers are shown in Figure 5, and the thermal properties of the polymers are summarized in Table IV. In the plot, there are two humps due to the formation of the copolymer. The first hump is probably due to the degradation of the siloxane moiety, whereas the second degradation is due to the rigid imide linkage. The 5% weight loss of these polymers was in the temperature range of $434\text{--}460^\circ\text{C}$, whereas a 50% weight loss was observed in the temperature range above 500°C ; this indicated good thermal stability but was observed to be lower than that of the analogous homopolymers.¹⁹ The relatively low thermal stability of these polymers was due to the presence of weak aminopropyl silane linkers in the polymer chain.³⁶ All these polymers

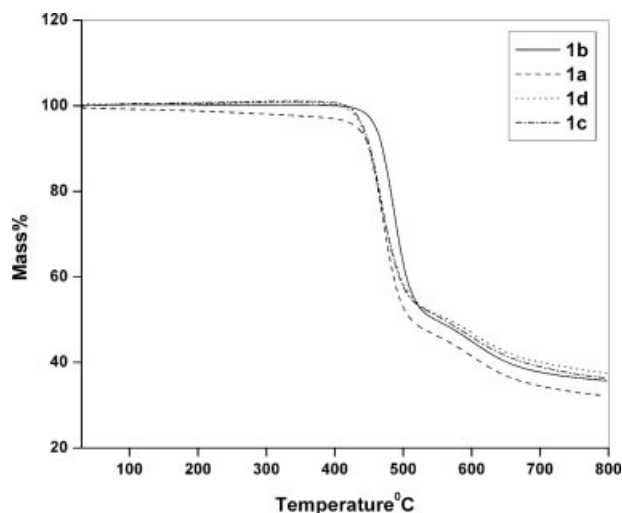


Figure 5 TGA thermograms of the polymers.

showed high char residues (>30 wt %) at 800°C under a nitrogen atmosphere.

Dynamic mechanical analysis (DMA) measurements

The T_g values taken from the $\tan \delta$ peaks at 1 Hz are given in Table IV. These values are comparable to the calorimetric T_g values. The polymers showed much lower storage modulus values than the analogous homopolymers, as reported earlier.¹⁹ The polymer films showed good storage modulus around 400 MPa at room temperature, which gradually decreased with an increase in temperature. The $\tan \delta$ values showed a maximum at a particular temperature, which in turn indicated the T_g values of the polymers, which were in good agreement with the T_g values indicated by the DSC plots. Representative DMA plots of films of polymers **1a** and **1b** are shown in Figure 6.

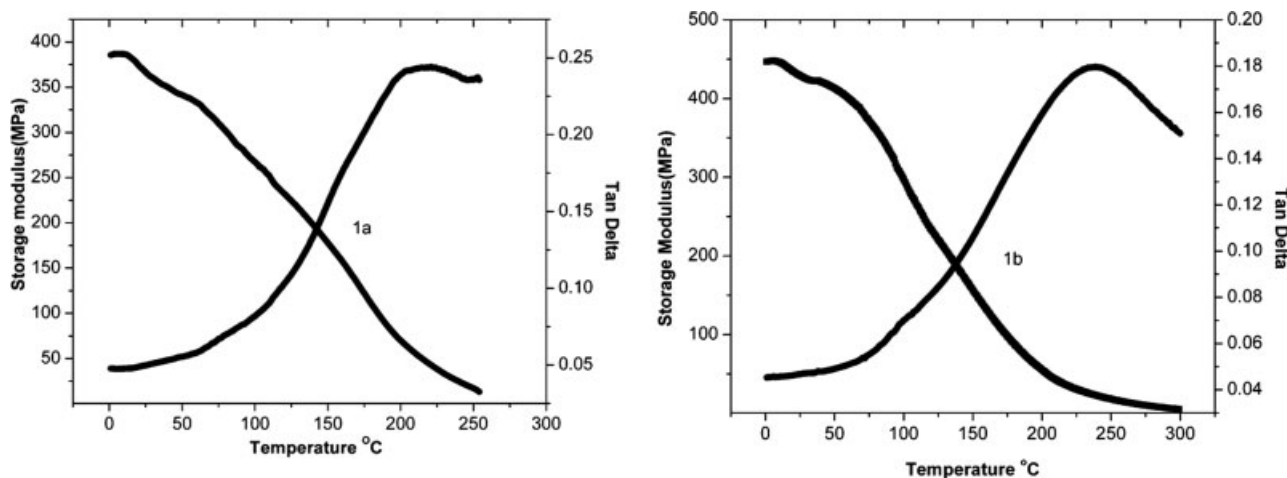
Figure 6 DMA plots of polymers **1a** and **1b**.

TABLE V
Mechanical and Water Absorption Behavior of Poly(imide siloxane)

Polymer	Tensile strength (MPa)	Storage modulus (MPa)	Elongation at break (%)	Young's modulus (GPa)	Water absorption after 72 h (%)
1a	28.3	385	73	0.61	0.04
1b	30.3	445	103	0.63	0.02
1c	23.3	447	12	0.55	0.05
1d	20.2	425	7	0.53	0.07

Mechanical properties

The mechanical properties of thin poly(imide siloxane) films are shown in Table V. In general, the mechanical properties of the poly(imide siloxane) films were excellent and exhibited tensile strengths and moduli of measurable values. The poly(imide siloxane) containing the most rigid quadriphenyl unit exhibited the highest tensile strength (up to 30 MPa) and also a high elongation at break (up to 103%; Fig. 7). It can also be observed from Table V that the polymers having a more extended geometry, **1a** and **1b**, had more elongation at break than the polymers having a less extended geometry. Moreover, the analogous homopolymers previously reported¹⁹ had less elongation at break with higher tensile strength at break and modulus. The films of **1a** and **1b** behaved like toughened thermoplastics with very high elongation at break. This was due to the incorporation of flexible siloxane units into the polymer backbone.

Water absorption study

Water absorption is an important parameter for materials to be used in electronic applications. A water absorption study of the poly(imide siloxane) was performed by the immersion of rectangular

samples (30 × 10 mm) in double-distilled water after the initial weight was taken at room temperature. The final weight was taken after 72 h, and the water absorption was calculated: Absorbed water (%) = [(Weight of the wet film – Weight of the dry film) / Weight of the dry film] × 100. Table V shows water uptake values as low as 0.02 wt % in the case of polymer **1b** and as low as 0.04 wt % in the case of polymer **1a**. These values were lower than those of the polymers containing pyridine (**1c**) and thiophene (**1d**) moieties, respectively. The water absorption values were 10 times lower than those observed for the respective homopolymers.¹⁹ The negligibly small water uptake of these polymers was possibly due to contributions from both fluorine and siloxane sequences³⁷ to the backbone of the polyimides. It will be interesting to check the contact angles of water on these films as reports indicate superhydrophobic films with a contact angle of approximately 160° obtained by the incorporation of polytetrafluoroethylene nanoparticles into a polydimethylsiloxane matrix.³⁸

Rheology

It is interesting to know how the apparent viscosity changes when shear rates (and stresses) are changing in a very wide range. To make this dependence more visual, logarithmic scales are frequently used.

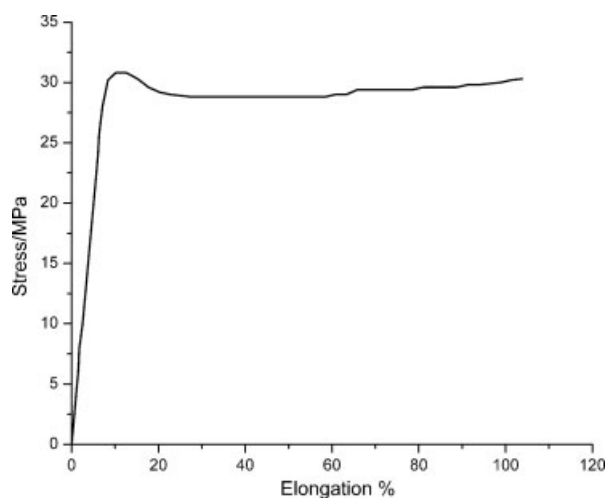


Figure 7 Representative stress–strain plot of polymer **1b**.

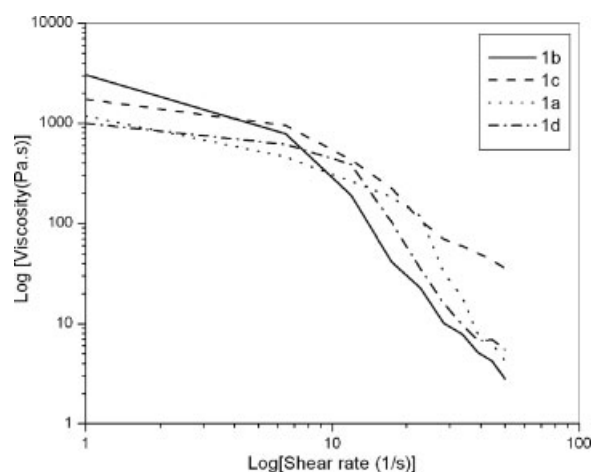


Figure 8 Flow curves of the polymers.

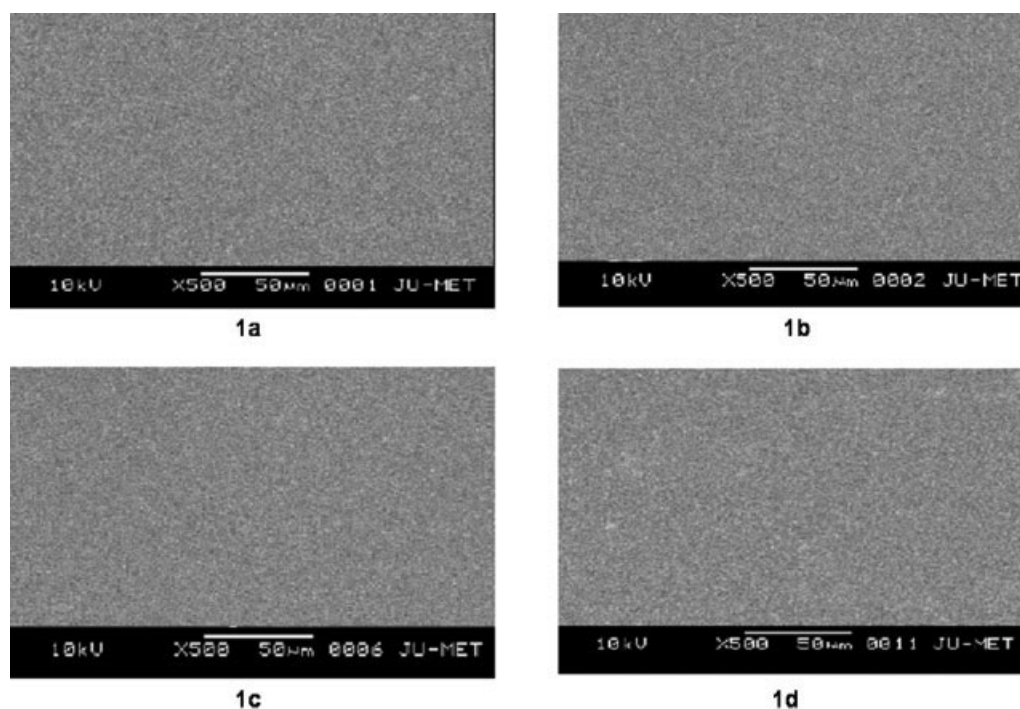


Figure 9 SEM micrographs of the polymers.

The flow curves of the polymers (Fig. 8) show very pronounced non-Newtonian flow as a gradual decrease of the apparent viscosity. The polymers showed low melt viscosity and hence good melt processability. At low shear rates, Newtonian behavior is observed, and the apparent viscosity corresponding to this region of the flow curves is called zero-shear or initial or maximum Newtonian viscosity. Then, the decrease of the apparent viscosity can be observed, being typical of non-Newtonian behavior. The whole decrease of the apparent viscosity exceeds 1000 times in comparison with the initial values. The initial Newtonian region in the flow curves appears in Figure 8 only as a hint; it may even be suspected that this branch does exist.

Surface morphology

The surface morphology of the four polymers was studied with SEM to observe the distribution of the siloxane moiety in the polymer backbone. Figure 9 shows the distribution of siloxane in the polyimides under consideration, indicating microphase separation. It can be observed from the SEM micrographs that the dispersed domains were nearly spherical, the domain size was relatively small, and the phase contrast was somewhat poor.

Dielectric properties

An analysis of the dielectric constant of polymer **1a** was completed. For this study, both sides of a poly-

mer film of **1a** (10 mm × 10 mm × 0.1 mm) were metalized with a coating of Au-Pd. The multifrequency-multitemperature capacitance values of the film were measured and were converted into dielectric constants. The dielectric spectra of polymer **1a** are shown in Figure 10. It shows a gradual decrease in the dielectric constant as the frequency of the measurement increased and temperature of the measurement decreased. The observed dielectric constant was as low as 2.38 at 1 MHz and 32°C; this value was reasonably lower than that of the analogous homopolymer.¹⁹

CONCLUSIONS

Four new poly(imide siloxane)s were prepared through a reaction of oxydiphthalic anhydride with different trifluoromethyl-substituted diamines, each with a 40% siloxane loading. The polymers were

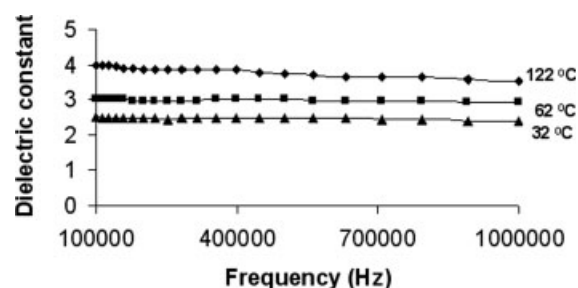


Figure 10 Dielectric spectra of polymer **1a**.

well characterized by thermal, mechanical, water-sorption, X-ray, and dielectric studies. The synthesized polymers exhibited very good solubility in different organic solvents. The resulting poly(imide siloxane)s were amorphous according to X-ray studies and had reasonably good thermal stability with respect to other polyimides. Because of the micro-phase morphology of the films, T_g of the polyimide matrix was ideally depressed only to a small extent. As expected, the polymers had low tensile strength but high elongation at break. The polymer films absorbed negligibly small amounts of water and showed a low dielectric constant for **1a**, whereas dielectric studies of the remaining polymers are under investigation. These polymers may find applications in high-temperature cable insulation and in gas-separation membranes.

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