

Thermal, Mechanical, and Dielectric Properties of Novel Fluorinated Copoly(imide siloxane)s

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Received 18 December 2007; accepted 27 February 2008

DOI 10.1002/app.28298

Published online 6 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Eight new poly(imidesiloxane)s copolymers have been prepared by one-pot solution imidization method. The polymers are made by the reaction of bisphenol-A dianhydride (BPADA) with four different fluorinated diamines and amino-propyl terminated polydimethylsiloxane (APPS). The polymers are named as 1a, 1b, 1c, and 1d, respectively, with a siloxane loading of 40 wt %. The second series of polymers where siloxane loading is 20 wt % were named as 1e, 1f, 1g, and 1h. The resulting polymers have been well-characterized by GPC, IR, and NMR techniques. The proton NMR indicates the siloxane loading is about 36–38% for the first series of polymers 1a–1d and a loading of 17–18% for the series of

polymers 1e–1h. The films of these polymers showed low water absorption of 0.02% for the first series of polymers and 0.11% for the second series of polymers. Thermal, mechanical, and dielectric properties of these polymers have been evaluated and compared with their nonsiloxane analogues. Preliminary investigations of melt processability of these polymers were also investigated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2329–2340, 2008

Key words: fluorinated polyimides; poly(imide siloxane); thermal properties; mechanical properties; dielectric constant; rheological properties

INTRODUCTION

High-performance polymers such as polyimides can be attributed to their outstanding properties such as excellent thermal and thermo-oxidative stability, solvent resistance, mechanical and electrical properties.^{1–6} They are widely used in electronic and micro-electronic industries,^{7–10} aerospace fields^{11,12} as well as membranes for gas separation.¹³ To utilize the thermal stability of polyimides for further applications, and also to take advantage of other properties of these classes of polymers, such as high chain rigidity, packing density, and polar chain interactions, it is desirable to synthesize soluble and/or melt-processable variations. 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 thermal and chemical resistance due to the high electronegativity of fluorine atoms and low electron polarizability of C–F bonds.^{14–17} Incorporation of fluorine also enhances the solubility.¹⁸

Solubilizations have been tried by several means such as introduction of flexible linkages,^{19,20} bulky substituents,^{21,22} or bulky units in the polymer back-

bone,^{23–25} noncoplanar,^{26,27} or alicyclic²⁸ monomers. Additionally, an incorporation of siloxane unit to polyimides and related polymers^{29–32} 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 properties to the substrate. Kuckertz et al.³³ first reported poly(imide siloxane), which was prepared from PMDA with various low molecular weight amine-terminated siloxane dimers. Summers³⁴ incorporated APPS with various ratios (5, 10, 20, and 40%) of different molecular weight ($M_n \sim 900$ – $10,000$ g/mol) into the 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 3,3' diaminodiphenylsulfone (3,3'-DDS)-based polyimide. Studies have also been done regarding incorporation of polydimethyl siloxane segment in the polymer backbone. Arnold et al.³⁵ have tried to incorporate varying amount of respective amount of siloxane in the polyimide backbone but incorporation has found to be less than that tried while investigation by Pechar et al.³⁶ have reported 22 and 41 wt % siloxane incorporation where they attempted 20 and 40 wt % incorporation, respectively. Sun et al.³⁷ 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.³⁸ investigated molecular mobility in relation to morphology in polyimide-poly(dimethylsilox-

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ane) hybrid networks (PI-PDMS) by employing dielectric techniques, including broadband dielectric relaxation spectroscopy and thermally stimulated depolarization currents, and to a lesser extent differential scanning calorimetry and equilibrium water sorption isotherm measurements. The modification of the siloxane segment did provide several desired improvements in the bulk and surface properties. Lai et al.^{39–41} synthesized poly(imide siloxane)s from Pyromellitic dianhydride (PMDA), 4,4'-oxydianiline (ODA), and oligomeric dimethylsiloxane (ODMS) and then utilized them in gas separation and pervaporation. Stern et al.⁴² 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 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.⁴³ 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.

In our previous work, while decreasing the siloxane incorporation in the polymer chain from 40% loading to 20% loading using ODPAs (*o*-diphthalic anhydride) as dianhydride there were solubility problem of the polymers during casting film.⁴⁴

In the present work, BPADA is chosen as dianhydride and diamines are the same fluorinated diamines. Here we have incorporated two different levels of siloxane, 20 and 40 wt % and the properties of the resulting polymers have been investigated thoroughly.

EXPERIMENTAL

General consideration

Carbon, hydrogen, and nitrogen of the compounds were analyzed by pyrolysis method. ¹H-NMR and ¹³C-NMR were recorded on a Bruker 500 MHz instrument (Switzerland) using CDCl₃ as solvent. IR spectra of the polymer films were recorded with a Netzsch (Germany) 870 FTIR Spectrophotometer instrument. DSC measurements were made on a QC 1000, TA instrument at a heating/cooling rate of 20°C/min under nitrogen. Glass transition temperature (T_g) was taken at the middle of the step transition in the second heating run. Thermal decomposition behavior of these polymers was measured on Perkin-Elmer (Pyris Diamond) at a heating rate of 10°C/min under nitrogen. Dynamic mechanical ther-

mal analysis was performed on a TA Instrument DMA-2980 (New Castle, DE) under tension mode on thin film samples at a heating rate of 10°C/min and were run at a frequency of 1 Hz. Mechanical properties such as tensile strength and elongation at break of the thin polymer films (30 × 0.1 mm) were elongated at room temperature on a Hounsfield (UK) H10KS-0547 instrument under strain rate of 5%/min of the sample length. Viscosity was measured by Ubbelohde type of viscometer at 30°C. 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, and a VE 3580 RI detector. 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. Dry specimens were made by keeping the samples at 80°C for overnight under high vacuum and water absorption of the films was measured by a balance of sensitivity of 10⁻⁶ g after immersing the films into double distilled water for 24 h at 30°C. Dielectric constant of the polyimide films was measured by parallel plate capacitor method with a HIOKI 3535 LCR Hi Tester from 100 KHz to 1 MHz at a temperature of 30°C. Scanning electron microscopy (SEM) was used to study the morphology by JSM-6360 of JEOL Co. Atomic Force Microscopy (AFM) was studied by NT-MDT (Solver-Pro, Russia) in contact mode. Rheology behavior of the films was studied by using AR-1000 Rheometer.

Starting materials

All reagents were purchased from Aldrich (USA), Gelest (USA) and used as received unless otherwise noted. Bis phenol-A-dianhydride (BPADA 97%, Aldrich, USA) was heated at 120°C overnight prior to use. Aminopropyl terminated polydimethylsiloxane (APPS) of block length $n = 8.31$, was purchased from Gelest. 1,2-Dichlorobenzene (ODCB) (E. Merck, India) was used as received. Methanol was purchased from Ranbaxy Fine Chem, India. The diamine monomers used in this investigation were prepared using the procedure reported in our previous articles.^{45–47}

Polymerization

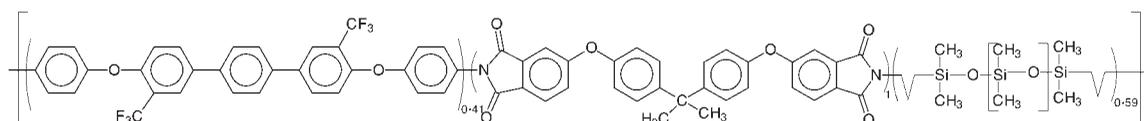
The polymerization reactions were conducted by the reaction of BPADA and two different diamines in a random fashion. In all the cases, 1 mol of BPADA and mixture of two diamines which add up to 1 mol is presented in the subscript of all the polymeric structures 1a–1h, respectively. The reactions were

conducted under constant flow of nitrogen. A representative polymerization procedure with 40% loading of APPS is as follows.

In a 50-mL, three-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-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 in 500 mL methanol. The resulting precipitate was then collected by filtration and was dried under vacuum at 80°C for overnight. Measured amount of polymer was then solubilized in dichloromethane and film was then casted on to a petridish and was then heated in a vacuum oven 120°C overnight. Transparent pale-yellowish colored films were obtained in all eight polymers, respectively.

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

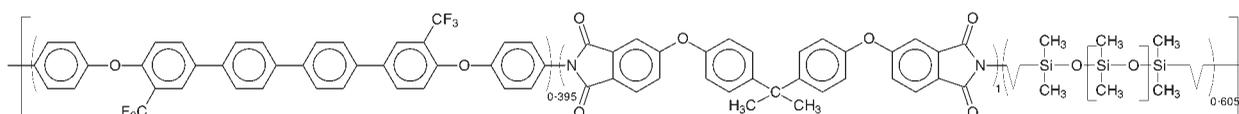


Anal. calc. for (C_{58.29115} H_{70.9574} F_{2.46} O_{12.3129} N₂ Si_{6.0829})_n (1232.72 g mol⁻¹)_n : C, 58.29; H, 5.80; N, 2.27 Found : 60.0; H, 5.75; N, 2.49.

IR (KBR) (cm⁻¹): 2962(—CH₃ group present in APPS); 1773 and 1716 (asymmetric and symmetric —CO— stretch); 1601 (C=C ring stretching band); 1506, (band due to C—F absorption); 1392 (asymmetric C—O—C stretch); 1084, 1021 (Si—O—Si

stretching); 800 (Si—C). ¹H-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.

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



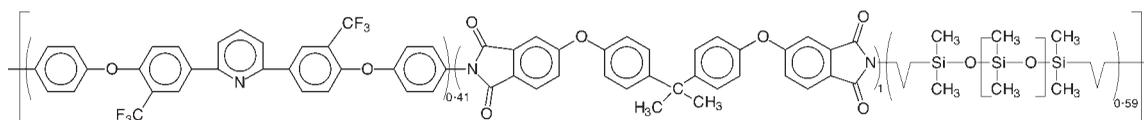
Anal. calc. for (C_{62.1151} H_{73.3753} F_{2.37} O_{12.4225} N₂ Si_{6.2375})_n (1267.04 g mol⁻¹)_n : C, 58.88; H, 5.83; N, 2.21 Found : C, 59.22; H, 5.76; N, 2.59.

IR (KBR) (cm⁻¹): 3477(—N < stretch); 3069 (aromatic C—H stretching); 2962(—CH₃ group present in APPS); 1773 and 1716 (asymmetric and symmetric —CO— stretch); 1602 (C=C ring stretching band); 1504, (band due to C—F absorption); 1389 (asymmetric C—O—C stretch); 1083, 1020 (Si—O—Si

stretching); 800 (Si—C). ¹H-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.

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



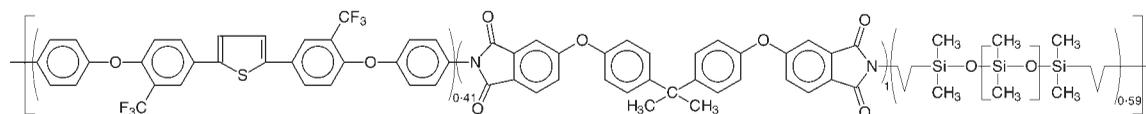
Anal. calc. for $(C_{59.4158} H_{70.5474} F_{2.46} O_{12.4225} N_{2.41} Si_{6.0829})_n$ ($1234.88 \text{ g mol}^{-1}$) $_n$: C, 57.79; H, 5.75; N, 2.73 Found: C, 58.23; H, 5.69; N, 3.10

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

(Si—C). $^1\text{H-NMR}$ (CDCl_3): 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).

$^{13}\text{C-NMR}$ (CDCl_3): 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.

Poly (imide siloxane) – 1d_{40wt% APPS}



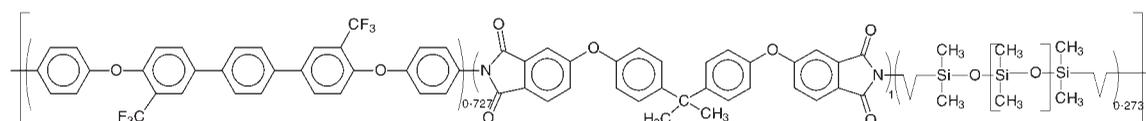
Anal. calc. for $(C_{59} H_{70.1374} F_{2.46} O_{12.3129} N_2 Si_{6.0829} S_{0.41})_n$ ($1235.19 \text{ g mol}^{-1}$) $_n$: C, 57.37; H, 5.72; N, 2.26 Found: C, 58.21; H, 5.32; N, 2.55.

IR (KBR) (cm^{-1}): 2962 (—CH₃ group present in APPS); 1774 and 1717 (asymmetric and symmetric —CO— stretch); 1601 (C=C ring stretching band); 1504, (band due to C—F absorption); 1389 (asymmetric C—O—C stretch); 1085, 1022 (Si—O—Si stretching); 801 (Si—C). $^1\text{H-NMR}$ (CDCl_3): 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).

$^{13}\text{C-NMR}$ (CDCl_3): 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.

Poly (imide siloxane) – 1e_{20wt% APPS}



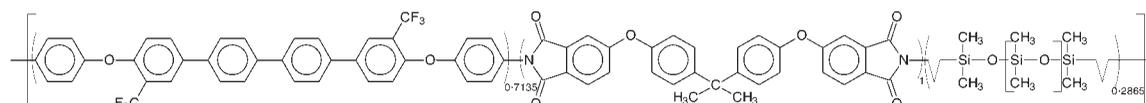
Anal. calc. for $(C_{61.5312} H_{53.2497} F_{4.362} O_{9.9956} N_2 Si_{2.8146})_n$ ($1142.61 \text{ g mol}^{-1}$) $_n$: C, 64.68; H, 4.69; N, 2.45 Found: C, 64.93; H, 4.21; N, 2.63.

IR (KBR) (cm^{-1}): 2963 (—CH₃ group present in APPS); 1777 and 1722 (asymmetric and symmetric —CO— stretch); 1618 (C=C ring stretching band); 1506, (band due to C—F absorption); 1377 (asymmetric C—O—C stretch); 1080, 1015 (Si—O—Si stretching); 800 (Si—C). $^1\text{H-NMR}$

(CDCl_3): 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).

$^{13}\text{C-NMR}$ (CDCl_3): 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.

Poly (imide siloxane) – 1f_{20wt% APPS}



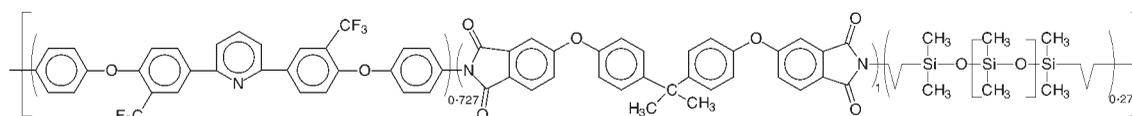
Anal calc. for $(C_{65.7396} H_{56.8578} F_{4.281} O_{10.0943} N_2 Si_{2.9538})_n$ ($1200.74 \text{ g mol}^{-1}$): C, 65.76; H, 4.77; N, 2.33 Found : C, 65.40; H, 4.63; N, 2.46.

IR (KBR) (cm^{-1}): 3477(—N < stretch); 2961(—CH₃ group present in APPS); 1777 and 1723 (asymmetric and symmetric —CO— stretch); 1600 (C=C ring stretching band); 1503, (band due to C—F absorption); 1376 (asymmetric C—O—C stretch); 1079, 1015 (Si—O—Si stretching); 799 (Si—C). ¹H-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.

Poly (imide siloxane) – 1g_{20wt%} APPS



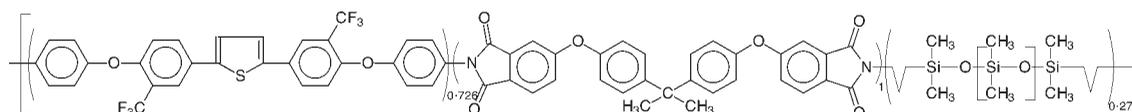
Anal calc. for $(C_{60.8042} H_{52.5227} F_{4.362} O_{9.9956} N_{2.727} Si_{2.8146})_n$ ($1143.33 \text{ g mol}^{-1}$): C, 63.87; H, 4.63; N, 3.34 Found : C, 63.55; H, 4.29; N, 3.33.

IR (KBR) (cm^{-1}): 2963(—CH₃ group present in APPS); 1777 and 1723(asymmetric and symmetric —CO— stretch); 1610 (C=C ring stretching band); 1500, (band due to C—F absorption); 1378 (asymmetric C—O—C stretch); 1080, 1016 (Si—O—Si stretching); 802 (Si—C). 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.

Poly (imide siloxane) – 1h_{20wt%} APPS



Anal calc. for $(C_{60.0738} H_{51.8536} F_{4.356} O_{10.0029} N_2 Si_{2.8249} S_{0.726})_n$ ($1147.27 \text{ g mol}^{-1}$): 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— stretch); 1602 (C=C ring stretching band); 1506, (band due to C—F absorption); 1377 (asymmetric C—O—C stretch); 1082, 1019 (Si—O—Si stretching); 801 (Si—C). ¹H-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.

RESULTS AND DISCUSSION

The reaction scheme and polymer structures are shown in Figure 1. The polymers were prepared by conventional one-pot solution imidization method. A high boiling nonpolar solvent is preferred one; in the present synthesis, ODCB was used as solvent with a solid content of 20 wt %. The reactants; diamines, and dianhydrides were mixed in a random fashion, the polymerization temperature was raised slowly to 180°C and continued for 6 h at 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. After completion of 6 h at 180°C, the reaction temperature was brought down to room temperature and the polymer solution was precipitated in 500 mL methanol. The fibrous product

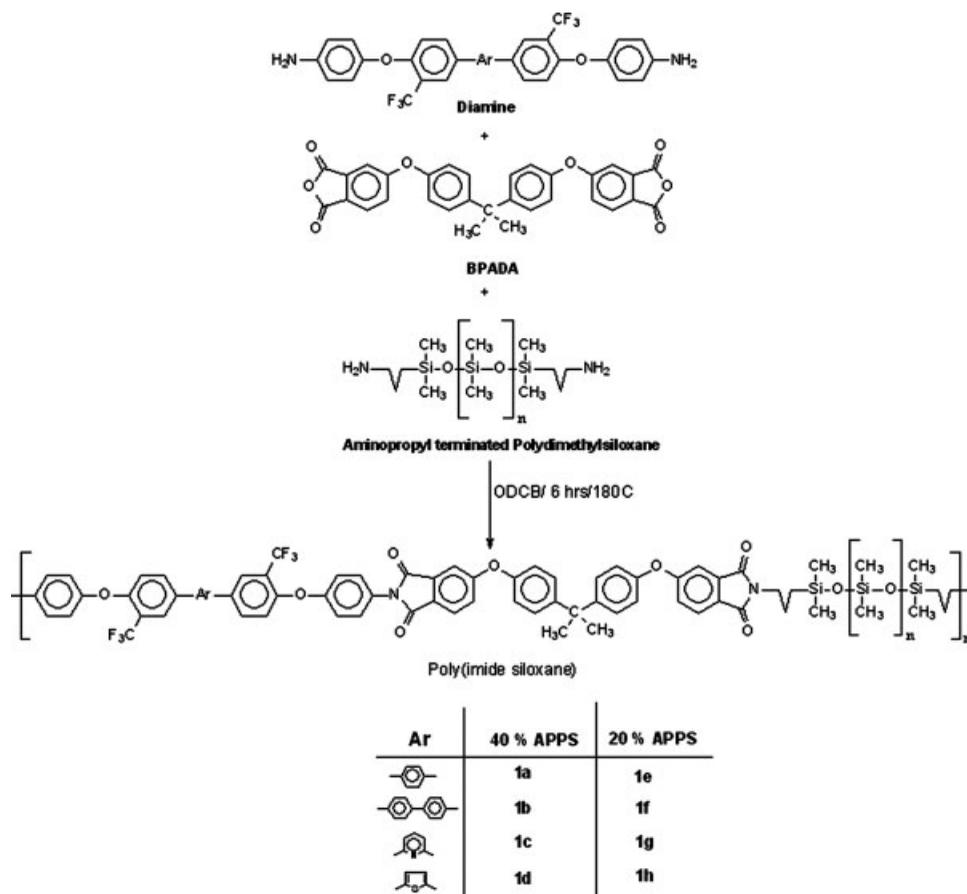


Figure 1 Reaction scheme and chemical structures of the poly(imidesiloxane)s.

obtained was dried and dissolved in 20 mL dichloromethane and reprecipitated in excess methanol. The fibrous products obtained were dried at 80°C for overnight under vacuum and was used for further analysis. The inherent viscosities and molar masses of the poly(imidesiloxane)s are shown in Table I which indicates high molar masses. The polymer solutions (15 wt %) in dichloromethane were poured in flat bottom Petri dishes and the films were prepared by evaporating the solvent at a control rate at 30°C for overnight. The Petri dishes were kept in a vac-

uum oven and the temperature of the oven was slowly raised to 120°C and kept under continuous vacuum for overnight to remove any trace solvent.

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 II. These polymers exhibited very good solubility in common organic solvents such as *N*-methyl-2-pyrrolidinone (NMP), dimethylformamide (DMF), *N,N*-dimethyl acetamide (DMAc), tetrahydrofuran (THF), chloroform (CHCl₃), and dichloromethane (CH₂Cl₂) and was observed to be insoluble in DMSO and acetone. In comparison to the previous reported analogous homopolymers,⁴⁸ 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 to ease of the polymer to solvent attack. It was not possible to get soluble polymers with 20 wt % of siloxane loading when ODPA was used as dianhydride.⁴⁴ The polymers showed excellent solubility behavior with 20 wt % siloxane loading when BPADA is used as

TABLE I
Molecular Weight and PDI of the Polymers

| Polymer | η_{inh} (dL/g) | M_n (g/mol) | PDI |
|----------------------------|---------------------|---------------|------|
| 1a ₄₀ wt % APPS | 0.395 | 32,400 | 2.14 |
| 1b ₄₀ wt % APPS | 0.339 | 42,000 | 2.23 |
| 1c ₄₀ wt % APPS | 0.294 | 21,300 | 1.95 |
| 1d ₄₀ wt % APPS | 0.298 | 32,200 | 2.34 |
| 1e ₂₀ wt % APPS | 0.435 | 35,500 | 1.93 |
| 1f ₂₀ wt % APPS | 0.541 | 55,900 | 2.41 |
| 1g ₂₀ wt % APPS | 0.375 | 25,600 | 1.73 |
| 1h ₂₀ wt % APPS | 0.428 | 48,700 | 2.16 |

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

TABLE II
Solubilities of the Polymers

| Polymer | NMP | DMF | DMAc | DMSO | THF | CHCl ₃ | CH ₂ Cl ₂ | Acetone |
|----------------------------|-----|-----|------|------|-----|-------------------|---------------------------------|---------|
| 1a ₄₀ wt % APPS | + | + | + | – | + | + | + | – |
| 1b ₄₀ wt % APPS | + | + | + | – | + | + | + | – |
| 1c ₄₀ wt % APPS | + | + | + | – | + | + | + | – |
| 1d ₄₀ wt % APPS | + | + | + | – | + | + | + | – |
| 1e ₂₀ wt % APPS | + | + | + | – | + | + | + | – |
| 1f ₂₀ wt % APPS | + | + | + | – | + | + | + | – |
| 1g ₂₀ wt % APPS | + | + | + | – | + | + | + | – |
| 1h ₂₀ wt % APPS | + | + | + | – | + | + | + | – |

+, soluble at room temperature; –, insoluble at reflux.

dianhydride. This enhanced solubility in this series of polymers is attributed to the highly flexible nature of BPADA in comparison to ODPA. 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.

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 is due to the presence of methyl groups attached to silicon molecules in APPS. No detectable absorption band at 3400–2900 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, 1020, (Si–O–Si stretching), and 800 cm⁻¹ (Si–C) are the characteristic peaks of the siloxane group. ¹H-NMR spectra of the polymers also 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 III 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 though 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 our previous article.⁴⁴

Glass transition temperature versus 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 Gross Molecular Structure from Feed Ratio Versus the Protons Found from NMR

| Polymer | C-Aro | C-Ali | F-Aro | F-Ali | C-Ali/Aro | F-Ali/aro | A-Silo (%) |
|----------------------------|-------|-------|-------|-------|-----------|-----------|------------|
| 1a ₄₀ wt % APPS | 21.38 | 49.57 | 21.23 | 44.82 | 2.318 | 2.111 | 36.41 |
| 1b ₄₀ wt % APPS | 22.69 | 50.68 | 20.99 | 42.43 | 2.233 | 2.020 | 36.18 |
| 1c ₄₀ wt % APPS | 20.97 | 49.57 | 18.42 | 40.31 | 2.363 | 2.188 | 37.03 |
| 1d ₄₀ wt % APPS | 20.56 | 49.57 | 20.52 | 46.81 | 2.410 | 2.280 | 37.83 |
| 1e ₂₀ wt % APPS | 27.08 | 26.16 | 28.56 | 23.70 | 0.96 | 0.83 | 17.17 |
| 1f ₂₀ wt % APPS | 29.69 | 27.16 | 34.28 | 28.56 | 0.91 | 0.84 | 18.21 |
| 1g ₂₀ wt % APPS | 26.35 | 26.16 | 27.34 | 23.51 | 0.99 | 0.86 | 17.32 |
| 1h ₂₀ wt % APPS | 25.61 | 26.23 | 24.95 | 22.17 | 1.024 | 0.89 | 17.34 |

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 aliphatic/aromatic protons, F-Ali/Aro, found ratio of aliphatic/aromatic protons calculated from integrated peaks, A-silo (%), actual wt % incorporation of siloxane in the polymer structure = [F-Ali/Aro/C-Ali/Aro] × % Incorporation × 100.

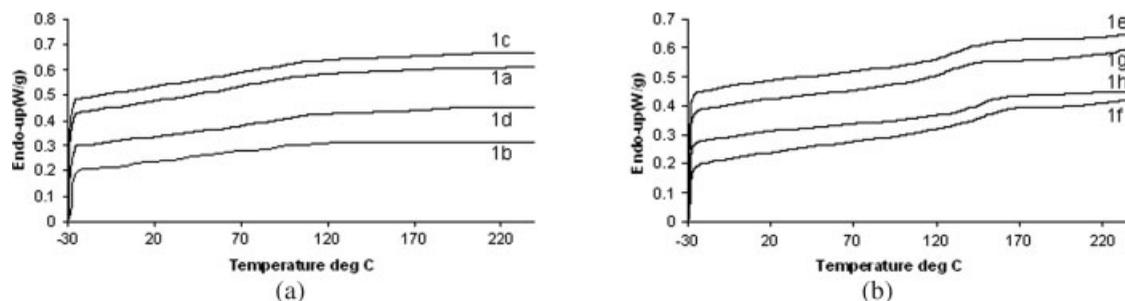


Figure 2 (a) DSC plots of polymers 1a–1d, (b) DSC plots of polymers 1e–1h.

These polymers show glass transition temperature, which indicates amorphous or glassy morphology. DSC curves of the polymers are shown in Figure 2(a,b) indicating glass transition temperatures of poly(imide siloxane)s with 40 and 20% siloxane loading, respectively. The glass transition values of the synthesized poly(imide siloxane)s are summarized in Table IV. In comparisons to the poly(imidesiloxane)s synthesized from ODP, these polymers showed a marked decrease in the T_g values probably due to two ether linkages present in the BPADA hence greater flexibility leading to lower glass transition temperatures. Compared to the homo poly(etherimide)s synthesized from BPADA,⁴⁸ these poly(imide siloxane)s showed lower glass transition temperature and as expected the glass transition temperatures decreased as the siloxane loading is increased. This gives a scope of manipulation of glass transition temperatures of the homopolymers for a suitable application.

Thermal stability

The thermal properties of the copolymers were evaluated by TGA. The TGA thermograms of the polymers are shown in Figure 3(a,b) and the thermal properties of the polymers are summarized in Table IV. 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 tem-

perature. As expected the co-polymers has lower thermal stability than their corresponding homopolymers.⁴⁸ The low thermal stability of these polymers is due to the presence of weak aminopropyl silane linkers in the polymer chain.³⁶ Compared to all the polymers, polymer 1b and 1f have been observed to show greater thermal stability in nitrogen due to the presence of rigid quadriphenyl unit in the polymer structure.

DMA measurements

The T_g s taken from the $\tan \delta$ peaks at 1 Hz are given in Table IV. The $\tan \delta$ 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 comparison 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 1a–1d and 1e–1h are shown in Figure 4(a,b), respectively. The polymers 1e–1h containing 20 wt % siloxane loading have good storage modulus values and are observed to be higher than the polymers 1a–1d which is obvious because flexibility gets reduced by less siloxane incorporation.

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 are excellent and exhibited tensile strength and modulus of measurable values. Compared to the previously reported poly(imide siloxane)s,⁴⁴ 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. The poly(imide siloxane), 1b containing most rigid quadriphenyl unit with 40 wt % APPS loading exhibited

TABLE IV
Thermal Properties of the Poly(siloxane)etherimides

| Polymer | DSC T_g (°C) | DMA ($\tan \delta$) T_g (°C) | T_d (°C) 5% weight loss in N ₂ | Char residue at 800°C in N ₂ |
|----------------------------|-------------------|--|---|--|
| 1a ₄₀ wt % APPS | 73.7 | 106 | 448 | 26.95 |
| 1b ₄₀ wt % APPS | 107 | 114 | 453.2 | 30.11 |
| 1c ₄₀ wt % APPS | 68.9 | 110 | 447.7 | 30.20 |
| 1d ₄₀ wt % APPS | 84.6 | 107 | 448.1 | 28.91 |
| 1e ₂₀ wt % APPS | 131.9 | 146 | 452.3 | 45.10 |
| 1f ₂₀ wt % APPS | 143.1 | 161 | 459 | 44.67 |
| 1g ₂₀ wt % APPS | 125.5 | 150 | 453.5 | 45.22 |
| 1h ₂₀ wt % APPS | 143.7 | 151 | 458.1 | 46.10 |

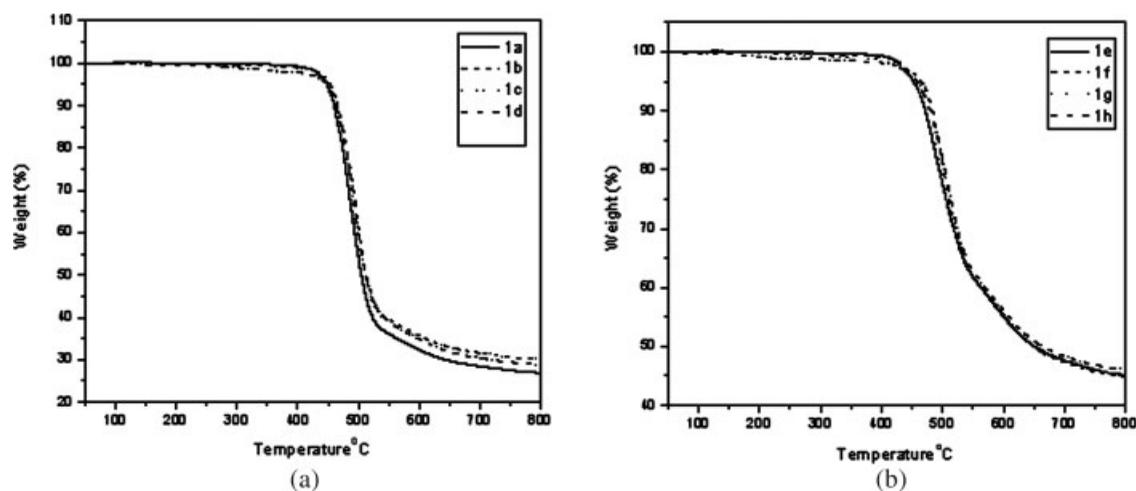


Figure 3 (a) TGA plots of polymers 1a–1d, (b) TGA plots of polymers 1e–1h.

highest tensile strength up to 24 MPa and also high elongation at break up to 144% while the polymer 1f 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 5 shows the Stress - Strain plots of the polymers (1a–1d) containing 40 wt % siloxane loading. Tensile strength values of the newly synthesized poly(imide siloxane)s are however lower when compared with the respective homopolymers⁴⁸ which is due to the incorporation of flexible amino-propyl 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.⁴⁸ 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, it is expected that the siloxane loading will affect great extent to the impact resistance of these polymers.

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)s were done by immersing rectangular pieces of samples (30 × 10 mm) in double distilled water after taking the initial weight at room temperature. Final weight was taken after 24 h and % water absorption was calculated. Table V shows the water uptake values as low as 0.02% in case of the polymer (1b) containing APPS content of about 40 wt % and as 0.11% for polymer (1f) containing APPS content of about 20 wt % and are lesser compared to the correspond-

ing homopolymers⁴⁸ which is in the range of 0.19–0.30%. Negligible small water uptake of these polymers is possibly due to the contribution both from fluorine and siloxane sequences⁵⁰ 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 observed from the Table V is also pronounced with the increase in siloxane loading from 20 to 40 wt %. This is probably due to the combined effect of fluorine as well as siloxane units present in the polymer backbone.

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 6 shows the distribution of siloxane in the polyimidesiloxane)s 1a and 1e indicating microphase 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 1a compared to 1e due to greater siloxane loading therein. Figure 7 shows the representative AFM image of polymer 1b showing two-dimensional and three-dimensional view. AFM image shows surface roughness of about 120 nm.

Rheology

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 8 showed very pronounced non-

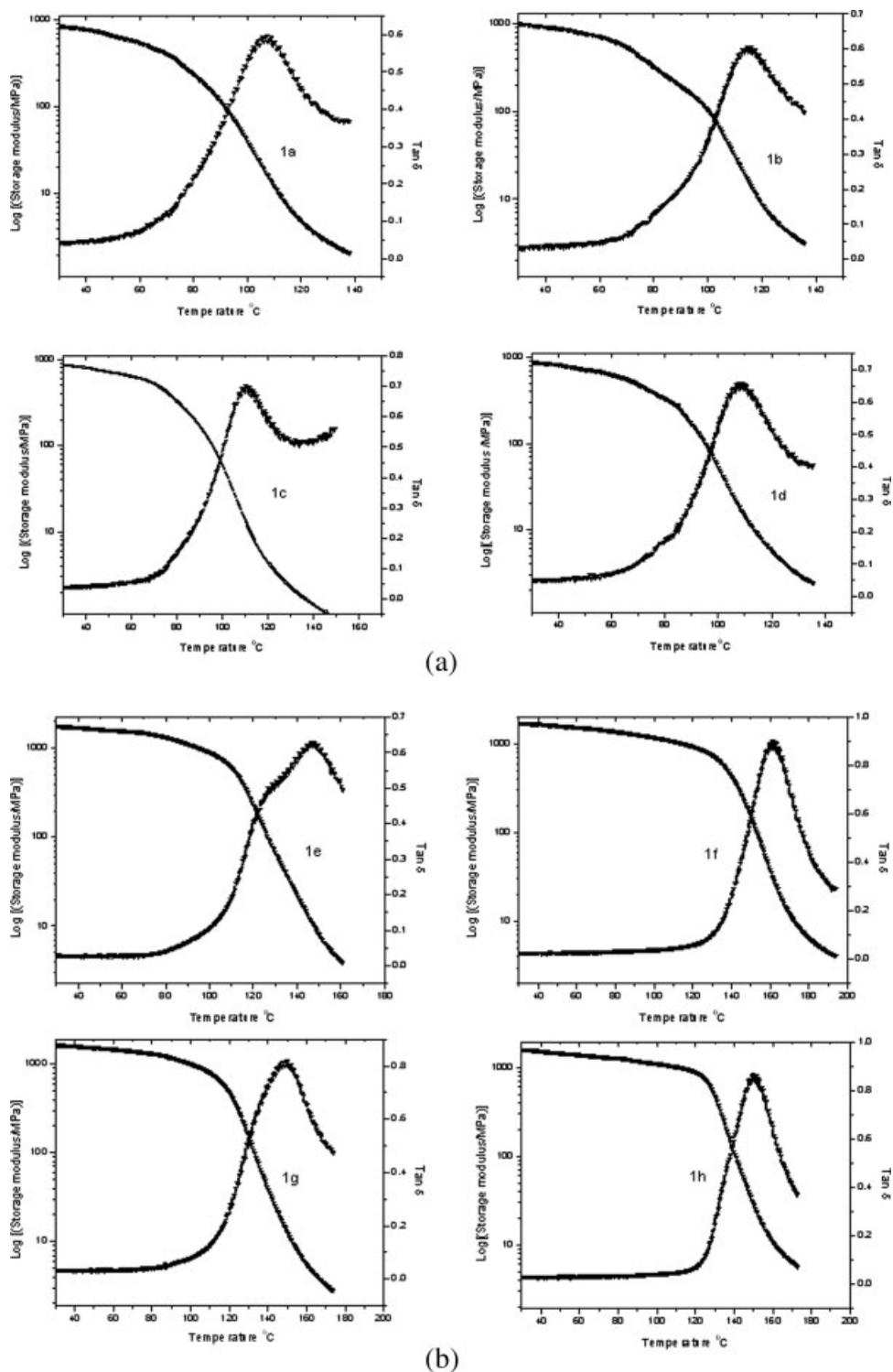


Figure 4 (a) DMA plots of polymers 1a–1d, (b) DMA plots of polymers 1e–1h.

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

| Polymer | Tensile strength (MPa) | Storage modulus (MPa) at 40°C | Elongation at break (%) | Young's modulus (MPa) | Water absorption (%) after 24 h | Dielectric constant at 1 MHz |
|----------------------------|------------------------|-------------------------------|-------------------------|-----------------------|---------------------------------|------------------------------|
| 1a ₄₀ wt % APPS | 18.60 | 772 | 90 | 750 | 0.03 | 2.39 |
| 1b ₄₀ wt % APPS | 24.27 | 918 | 144 | 890 | 0.02 | 2.43 |
| 1c ₄₀ wt % APPS | 22.21 | 748 | 63 | 730 | 0.06 | 2.56 |
| 1d ₄₀ wt % APPS | 19.82 | 810 | 90 | 833 | 0.08 | 2.59 |
| 1e ₂₀ wt % APPS | 51.00 | 1666 | 30 | 1010 | 0.15 | 2.71 |
| 1f ₂₀ wt % APPS | 57.00 | 1723 | 37 | 1230 | 0.11 | 2.63 |
| 1g ₂₀ wt % APPS | 44.00 | 1595 | 25 | 1260 | 0.17 | 2.93 |
| 1h ₂₀ wt % APPS | 48.40 | 1522 | 18 | 1300 | 0.20 | 3.06 |

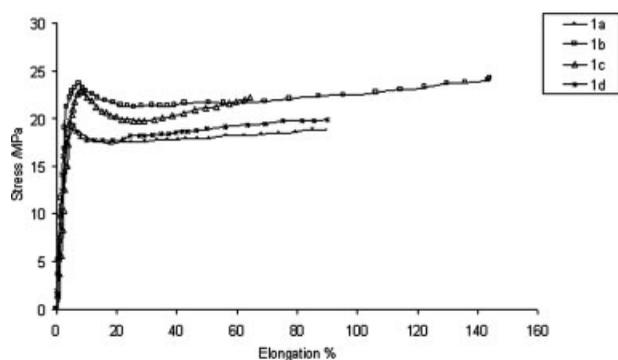


Figure 5 Representative stress-strain plot of the polymers 1a–1d.

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 polymer showed low melt viscosity and hence good melt processability. At low shear rates, Newtonian behavior is observed and apparent vis-

cosity 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.

CONCLUSIONS

Eight new poly(imide siloxane)s were prepared on reaction of bis phenol-A-di(phthaleic anhydride) with four different trifluoromethyl- substituted diamines with two different level of siloxane loading (40 and 20%). The polymers were well characterized by their spectroscopy, thermal, mechanical, water sorption, dielectric, and rheology studies. The synthesized polymers exhibited very good solubility in different organic solvents. The resulting poly(imide siloxane)s are amorphous as reported and reasonably good thermal stability. The polymers have low tensile strength but high elongation at break with increase in siloxane loading. The polymer films absorb negligibly small amount of water and show low dielectric constant depending on the incorpora-

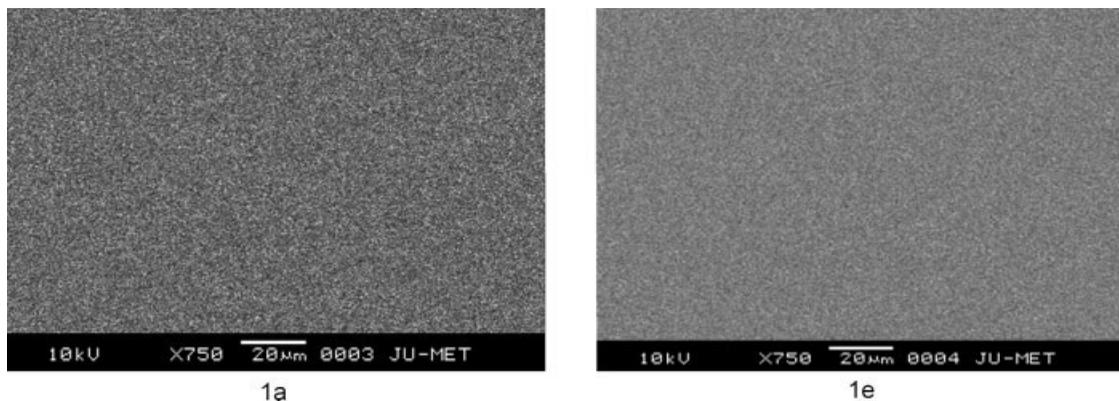


Figure 6 SEM micrographs of the polymers.

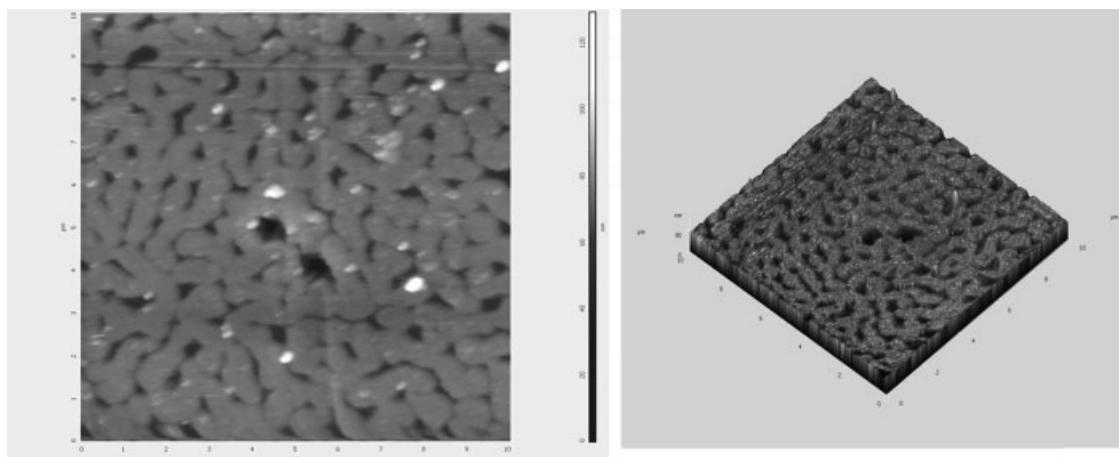


Figure 7 AFM image of polymer 1b showing two-dimensional view and three-dimensional view.

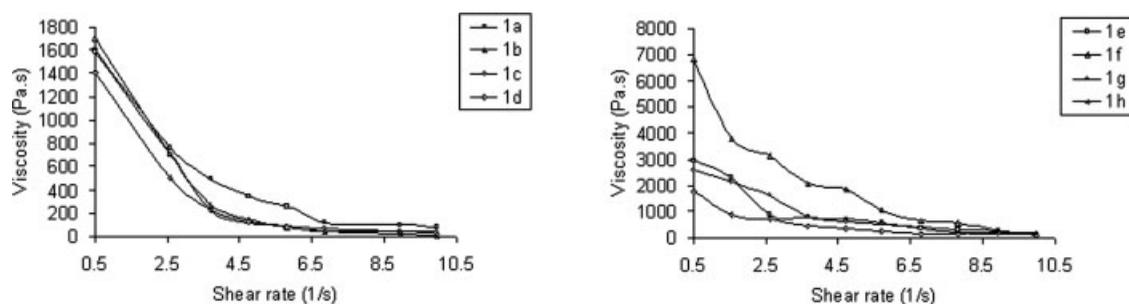


Figure 8 Rheology behavior of the polymers.

tion of siloxane. These polymers may find application in high temperature cable and in gas separation membranes.

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