

# Synthesis, Characterization, and Properties of New Siloxane Grafted Copolyimides

Anindita Ghosh,<sup>1,\*</sup> Susanta Banerjee,<sup>2</sup> De-Yi Wang,<sup>1,3</sup> Hartmut Komber,<sup>1</sup> Brigitte Voit<sup>1</sup>

<sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany

<sup>2</sup>Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

<sup>3</sup>College of Chemistry, Sichuan University, Chengdu 610064, China

Received 10 February 2011; accepted 18 May 2011

DOI 10.1002/app.34927

Published online 1 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Three new siloxane containing grafted copolyimides have been prepared by one-pot solution imidization technique. The polymers are made by the reaction of 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BPADA) with commercially available diamine 4,4'-oxydianiline (ODA) with variation of silicon containing diamine, namely 3,5-diaminobenzoate terminated polydimethylsiloxane (DBPDMS), as a comonomer to 10, 20, and 30 wt %. The films of the polymers were prepared by casting the polymer solution in dichloromethane. The polymers have been well-characterized by GPC, IR, and NMR techniques. Thermal stabilities and decomposition behavior of the copolyimides were studied

by DSC and TGA. The water contact angle values of the films indicate hydrophobic nature of the polymers. Thermal, flame retardant, mechanical, and surface properties of these polymers have been compared with the homopolyimide and with polyimides where polysiloxane is incorporated in the main chain. DSC revealed melting of the grafted siloxane chain at sub-ambient temperature and a glass transition corresponding to the main polymer chain above 200°C. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2959–2967, 2012

**Key words:** polyimides; graft copolymers; polysiloxane; thermal properties; mechanical properties

## INTRODUCTION

High-performance polymers such as polyimides are well known for their excellent thermal and thermo-oxidative stability, solvent resistance, mechanical, and electrical properties.<sup>1,2</sup> The polysiloxane components impart a number of interesting properties to the polymeric system including enhanced solubility, gas permeability, reduced water sorption, good thermal and ultraviolet stability, resistance to degradation in aggressive oxygen environment, impact resistance, and modified surface properties.<sup>3,4</sup>

The technologies for surface modification of polymers or regulation of the polymer surface interaction with other substances have been of prime importance in polymer applications from the advent of polymer industries. A variety of technologies have been proposed for improving surface properties of polymers,

one of them being among them is the surface grafting of polymers.<sup>5–7</sup> It offers versatile means for incorporating new functionalities into existing polymers. Researchers<sup>8–10</sup> have reported polyimides with grafted poly(dimethylsiloxane) for numerous applications, including gas separation and pervaporation.

Silicon-containing compounds are also considered to be one of the “environmentally friendly” flame retardant materials.<sup>11</sup> They can segregate onto the surface of the material during fire due to their low surface energy forming a barrier layer. Research has shown that the addition of relatively small amount of silicon compounds to various polymeric materials can significantly improve their flame retardancy, through both char forming in the condensed phase and by trapping of active radicals in the vapor phase.<sup>12–15</sup> Silica-carbon compounds can form a protective silica layer and protect the polymer residue from further thermal decomposition at high temperatures.

In the present study we report the successful one pot synthesis of three new random copolymers synthesized from 4,4'-(4,4'-isopropylidenediphenoxy)-bis(phthalic anhydride) (BPADA) and 4,4'-oxydianiline (ODA) coupled with varying proportions of 3,5-diaminobenzoate terminated polydimethylsiloxane (DBPDMS) as a comonomer to 10, 20, and 30 wt %, respectively. The polymers are named as **1a**, **1b**, and **1c**, respectively. Structure–property relationships, solubility, and spectroscopic characteristics as well

\*Present address: Dow Chemical International Pvt. Ltd., R&D Center, Pune, Chemical & Polymer Synthesis (CPS) Sai Hira, Survey No. 30, Mundhwa, Pune – 411 036 India. E-mail: Ghosh@dow.com

Correspondence to: A. Ghosh (ghosh@ipfdd.de or andy.iitkgp@gmail.com).

Contract grant sponsor: Alexander von Humboldt Foundation.

as thermal, flame retardant, mechanical, and surface properties have been reported in this investigation. The properties of the siloxane grafted copolyimides have been compared with the previously reported linear poly(imide siloxane)s and with the homopolyimide without siloxane moiety.

## EXPERIMENTAL

### Methods

Elemental analysis was performed with a Vario MICRO Cube elemental analyzer (Elementar Analysensysteme GmbH, Hanau/Germany).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DRX 500 spectrometer using  $\text{CDCl}_3$  and  $\text{CDCl}_3/\text{trifluoroacetic acid-d 4 : 1 (v/v)}$ , respectively, as solvents and the solvent signal as internal standard ( $\delta(^1\text{H}) = 7.26$  ppm;  $\delta(^{13}\text{C}) = 77.0$  ppm). The spectra were measured immediately after dissolving the polymer because the polydimethylsiloxane chain decomposes under acidic conditions. IR spectra of the polymer films were recorded with a Vertex 80 V FTIR spectrophotometer instrument (Germany). Gel permeation chromatography was performed in THF with a PL MIXED-C column (pore size 5  $\mu\text{m}$ ) from Polymer Laboratories at a flow rate of 1.0  $\text{mL min}^{-1}$  with linear polystyrene as a standard, using multi angle laser light scattering (MALLS) Detector from Wyatt Technologies. HPLC-Pump 64 from Knauer was used for this investigation. The polymers **1a** and **1b** were not soluble in THF up to 50°C and hence the GPC of these polymers were carried out in *N,N*-dimethylacetamide; DMAc + 3  $\text{g L}^{-1}$  LiCl as solvent. Differential Scanning Calorimetry (DSC) measurements were carried out on a DSC Q 1000 of TA Instruments in the temperature range from -80 to 300°C at a scan rate of  $\pm 10$   $\text{K min}^{-1}$  under nitrogen atmosphere. Glass transition temperature ( $T_g$ ) was determined from the 2nd heating run to avoid the influence of residual solvent using the half step method. 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  $\text{K min}^{-1}$  and a frequency of 10 Hz. Thermal decomposition behavior of these polymers was investigated on a TGA Q 5000 of TA Instruments in the temperature range from room temperature to 800°C at a heating rate of 10  $\text{K min}^{-1}$  under nitrogen atmosphere. Microscale Combustion Calorimeter (MCC-1, FTT) was used to investigate flame retardancy of the polymers. In this system, about 5 mg samples were heated to 700°C at a heating rate of 1°C  $\text{s}^{-1}$  in a stream of nitrogen flowing at 80  $\text{cm}^3 \text{min}^{-1}$ . The volatile, anaerobic thermal degradation products in the nitrogen gas stream are mixed with a 20  $\text{cm}^3 \text{min}^{-1}$  stream of 20% oxygen and 80%

nitrogen prior to entering a 900°C combustion furnace. The mechanical properties of the copolymers were estimated by tensile testing at 5  $\text{mm min}^{-1}$ , load cell 100 N with a tensile tester Z010 from Zwick, Germany. The strain was measured optically with a Videotensometer NG from Messphysik, Austria. Using gauge lengths of about 3 mm at five different positions of each specimen the maximal local strain was estimated. The morphology of the free standing films of the grafted polymers was observed using Scanning electron microscope, Ultra plus (Carl Zeiss SMT, Germany) at a voltage of 2 kV, work distance 6.6 mm and aperture size 30  $\mu\text{m}$ . The sample coated on one side with platinum coating of 2 nm thickness was placed on epoxy matrix and cut with ultratome. Transmission electron micrographs of the skin samples were recorded on a TEM (CM 12, Philips) instrument, operating at an accelerating voltage of 120 kV. Water contact angle of the flat free standing films were measured using an OM40 micro instrument from Dataphysics, Filderstadt, Germany. The volume of the water droplets used for measurements was 2  $\mu\text{L}$ .

### Starting materials

All reagents were purchased from Aldrich and used as received unless otherwise noted. 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BPADA) was purchased from Aldrich, USA, and heated to 120°C overnight prior to use. The diamine monomer 4,4'-oxydianiline (ODA) was purchased from Fluka, USA (>99% purity) and was used as received. The diamine monomer DBPDMS used in this investigation was prepared in the same way using the procedure reported in our previous article.<sup>16</sup>

### Polymerization

The polymerization reactions were conducted by the reaction of BPADA and two different diamines in a random fashion under constant flow of nitrogen. A representative polymerization procedure for **1c** is as follows.

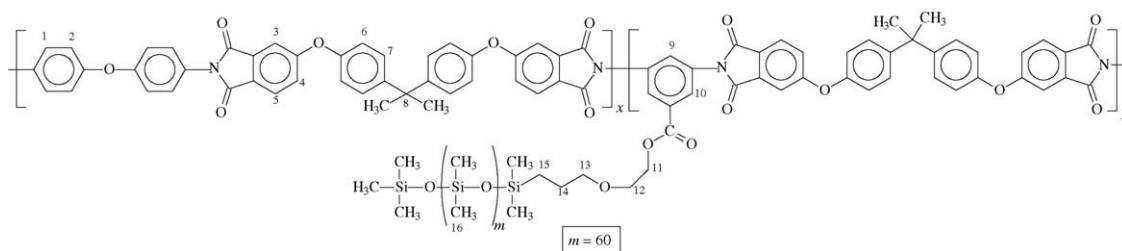
In a 50-mL three necked round-bottomed flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with 1.0288 g (1.98 mmol) BPADA, 0.3710 g (1.85 mmol) of ODA, 0.60 g (0.123 mmol) DBPDMS, and 20 mL of 1,2-dichlorobenzene was added in the flask. The 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 cov-

ered and the solvent was allowed to evaporate at a controlled rate at 25°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. Finally, the Petri dishes were placed in boiling water to remove the films from the substrate.

## Polymers 1a–1c

### Polymers 1a – 1c



Batch sizes and elemental analyses of siloxane grafted copolyimides

**1a.** BPADA, 1.3058 g (2.51 mmol); ODA 0.4940 g (2.47 mmol); DBPDMS, 0.20 g (0.04 mmol); ODCB, 20 mL.

Analytical calculation for **1a** with 0.8 mol % DBPDMS ( $C_{44}H_{31.04}O_{6.51}N_2Si_{0.49}$ )<sub>n</sub> (705.93 g mol<sup>-1</sup>): C, 74.85%; H, 4.44%; N, 3.96%; Found: C, 74.26 %; H, 4.23%; N, 3.43%.

**1b.** BPADA, 1.1672 g (2.24 mmol); ODA 0.4325 g (2.16 mmol); DBPDMS, 0.40 g (0.08 mmol); ODCB, 20 mL.

Analytical calculation for **1b** with 1.8 mol % DBPDMS ( $C_{45.25}H_{34.84}O_{7.15}N_2Si_{1.11}$ )<sub>n</sub> (752.44 g mol<sup>-1</sup>): C, 72.22%; H, 4.67%; N, 3.72%; Found: C, 71.94 %; H, 4.43%; N, 3.63%.

**1c.** BPADA, 1.0288 g (1.98 mmol); ODA 0.3710 g (1.85 mmol); DBPDMS, 0.60 g (0.123 mmol); ODCB, 20 mL.

Analytical calculation for **1c** with 3.2 mol % DBPDMS ( $C_{47}H_{40.16}O_{8.04}N_2Si_{1.98}$ )<sub>n</sub> (817.55 g mol<sup>-1</sup>): C, 69.04%; H, 4.96%; N, 3.42%; Found: C, 68.93 %; H, 5.05%; N, 3.98%.

### Spectroscopic data

IR (KBr) (cm<sup>-1</sup>): 3069 (weak, aromatic C–H stretching); 2962 (strong, aliphatic C–H stretching); 1777

(strong, asymmetric C=O of stretching imide); 1724 (very strong, symmetric C=O of stretching imide); 1618 (strong, C=C ring stretching band); 1376 (strong, asymmetric C–O–C stretching); 1078, 1014 (strong, Si–O–Si stretching); 801 (strong, Si–C stretching), 744 cm<sup>-1</sup> (C=O bending).

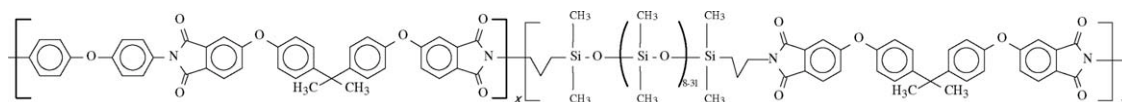
<sup>1</sup>H NMR (CDCl<sub>3</sub>/CF<sub>3</sub>COOD, 4 : 1 v/v): δ (ppm) = 8.21 (s, H<sup>10</sup>), 7.93 (d, H<sup>5</sup>), 7.87 (s, H<sup>9</sup>), 7.49 (s, H<sup>3</sup>), 7.39 (d, H<sup>4</sup>), 7.37 (d, H<sup>7</sup>), 7.35 (d, H<sup>1</sup>), 7.18 (d, H<sup>2</sup>), 7.06 (d, H<sup>6</sup>), 4.62 (t, H<sup>11</sup>), 4.00 (t, H<sup>12</sup>), 3.68 (t, H<sup>13</sup>), 1.77 (s, H<sup>8</sup>), 1.67 (m, H<sup>14</sup>), 0.52 (m, H<sup>15</sup>), 0.09 ppm (s, H<sup>16</sup>).

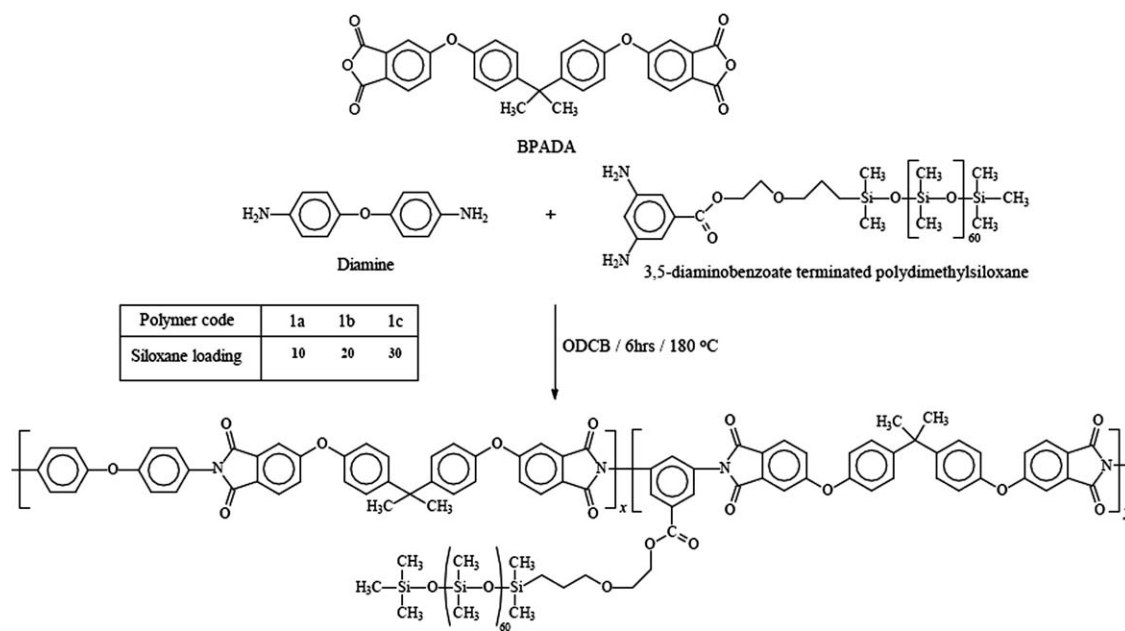
### Linear poly(imide siloxane) with 30 wt % loading

Batch size and elemental analysis of linear poly(imide siloxane) with 30 wt % loading polymerization has been done in a similar way as discussed in Polymerization section.

### Batch size

BPADA, 1.1112 g (2.135 mmol); ODA 0.2886 g (1.441 mmol); APPS, 0.6002 g (0.6940 mmol); ODCB, 20 mL.





**Scheme 1** Reaction scheme and structure of the siloxane grafted copolyimides.

Analytical calculation for  $(C_{47.7515}H_{49.4045}O_{9.7007}N_2-Si_{3.3507})_n$  ( $900.691 \text{ g mol}^{-1}$ )<sub>n</sub>: C, 63.67%; H, 5.53%; N, 3.11%; Found: C, 63.83 %; H, 5.67%; N, 3.43%.

### Spectroscopic data

IR (KBr) ( $\text{cm}^{-1}$ ): 2961 ( $-\text{CH}_3$  group present in APPS); 1780 and 1727 (asymmetric and symmetric  $-\text{CO}-$  stretch); 1626 ( $\text{C}=\text{C}$  ring stretching band); 1380 ( $\text{C}-\text{N}$  stretch); 1149 and 1093 ( $\text{Si}-\text{O}-\text{Si}$  stretching); 800 ( $\text{Si}-\text{C}$  stretching).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.90–7.00 (14.68H), 3.63 (s, 0.93H,  $-\text{CH}_2-\text{N}<$ ), 1.76 (s, 0.92 H,  $-\text{CH}_2-$ ), 0.91–0.54 (m 0.92H,  $-\text{CH}_2-\text{Si}$ ), 0.16–0.06 (m, 17.90 H,  $\text{Si}-\text{CH}_3$ ).

### Polymer solubility and molecular weight

The poly(imide siloxane) exhibited very good solubility 10% (w/v) in common organic solvents such as *N*-methyl-2-pyrrolidinone (NMP), dimethylformamide (DMF), *N,N*-dimethyl acetamide (DMAc), tetrahydrofuran (THF), chloroform ( $\text{CHCl}_3$ ), and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) and was observed to be insoluble in DMSO and acetone. The number average molecular weight ( $M_n = 54,200 \text{ g mol}^{-1}$ ) of the poly(imide siloxane) as obtained by GPC indicates formation of high molar mass with a polydispersity value of 2.34.

## RESULTS AND DISCUSSION

### Synthesis of polymers

The diamine monomer DBPDMS used in this investigation was prepared using the procedure reported in our previous article.<sup>16</sup>

The polymerization reaction scheme and the resulting polymer structures are shown in Scheme 1. The polymers were prepared by conventional one pot solution imidization method. A high boiling non-polar solvent is preferred; in the present synthesis 1,2-dichlorobenzene (ODCB) was used as solvent and the polymerization reactions were carried out with a solid content of 10 wt %. The reactants, diamines and dianhydride, were mixed, the polymerization temperature was raised to 180–190°C, and the reaction was continued for 6 h before cooling to room temperature and isolation of the product by precipitation in methanol. The fibrous product obtained was dried and purified by precipitation before further analysis. The molar masses of the silicon containing graft copolyimides determined by GPC are shown in Table I and indicate the formation of high molar mass products up to  $600,000 \text{ g mol}^{-1}$  ( $M_w$ ).

### Spectroscopy

The formation of the siloxane grafted polyimides were confirmed by FTIR spectra which showed absorption bands at about  $1777 \text{ cm}^{-1}$  ( $\text{C}=\text{O}$  asymmetric stretching),  $1726 \text{ cm}^{-1}$  ( $\text{C}=\text{O}$  symmetric stretching),  $1376 \text{ cm}^{-1}$  ( $\text{C}-\text{N}$  stretching), and  $722 \text{ cm}^{-1}$  ( $\text{C}=\text{O}$  bending) characteristic of the imide rings. The strong absorption bands at 1090, 1020  $\text{cm}^{-1}$  ( $\text{Si}-\text{O}-\text{Si}$  stretching) and  $800 \text{ cm}^{-1}$  ( $\text{Si}-\text{C}$ ) are characteristic for the siloxane group. The absence of detectable  $-\text{NH}$  stretching indicated the formation of high molar mass as evidenced from GPC data. The FTIR spectra of the siloxane grafted copolyimides are shown in Figure 1.

TABLE I  
GPC Molecular Weights and Solubility of the Siloxane Grafted Copolyimides

Polymer	$M_w$ (g mol <sup>-1</sup> )	PDI	NMP	DMF	DMAc	DMSO	THF	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	Acetone
1a	234,500 <sup>a</sup>	1.50 <sup>a</sup>	+	+	+	-	±	+	+	-
1b	673,200 <sup>a</sup>	1.40 <sup>a</sup>	+	+	+	-	±	+	+	-
1c	599,800	1.56	+	+	+	-	+	+	+	-

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

<sup>a</sup> Solvent DMAc + 3 g L<sup>-1</sup> LiCl.

<sup>1</sup>H NMR spectra of the polymers were recorded using CDCl<sub>3</sub> and CDCl<sub>3</sub>/CF<sub>3</sub>COOD (4 : 1, v/v) as solvent. The NMR spectra of all polymers recorded from CDCl<sub>3</sub> solutions are characterized by superposition of narrow and broadened signals for the aromatic protons. This effect is usually attributed to restricted mobility in polymers, e.g., as in microgels, but is surprising because both PDMS side chains and polyimide backbone should be well soluble in CDCl<sub>3</sub>. Addition of 20 vol % deuterated trifluoroacetic acid (TFA-d) resulted in narrow signals (Fig. 2) but, unfortunately, the PDMS side chains slowly degraded under acidic conditions. For this reason, the <sup>1</sup>H NMR spectra were taken immediately after TFA-d addition. The spectra confirm the expected polymer structures and the compositions determined from appropriate signal integrals are in good agreement with the feed compositions pointing to the fact that the PDMS grafted monomer DBPDMS is incorporated statistically into the polyimide structure. The NMR calculation indicates 0.8, 1.8, and 3.2 mol % siloxane loading in **1a**, **1b**, and **1c**, respectively that correspond to 9.7, 19.6, and 29.2 wt % siloxane loading whereas the attempted values were 10, 20, and 30 wt %. At the low level of siloxane loading the spectral peak area integration becomes difficult and the technique has overall 15% inaccuracy in analysis.

### Polymer solubility

The solubility of the resulting copolymers was investigated in different organic solvents. The results are

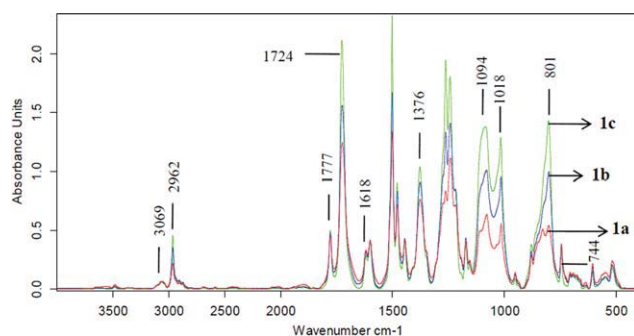


Figure 1 FTIR spectra of the siloxane grafted copolyimides (1a–1c). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

presented in Table I. It was attempted to obtain 10% (w/v) solutions of all polymers in several organic solvents. All the random copolymers 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), chloroform (CHCl<sub>3</sub>), and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), and were observed to be insoluble in dimethyl sulfoxide (DMSO) and acetone. Copolymers **1a** and **1b** were sparingly soluble in tetrahydrofuran (THF) but **1c** was soluble in THF at room temperature. For the copolymers **1a** and **1b** which were not soluble in THF up to 50°C, GPC measurements were performed in DMAc + 3 g L<sup>-1</sup> LiCl as solvent.

### Glass transition temperature versus polymer structure

DSC curves of the polymers and DBPDMS are shown in Figure 3, and the data are summarized in Table II. Interestingly, the siloxane grafted copoly(ether imide) shows two different transitions. The low temperature transition of the polymers at about -50°C is a typical side group melting transition of the grafted siloxane moiety coinciding with the melting of DBPDMS which increases in heat of transition ( $\Delta H_m$ ) with increasing siloxane content. On the other hand, the aromatic structure of the main chain induced a high glass transition temperature. The

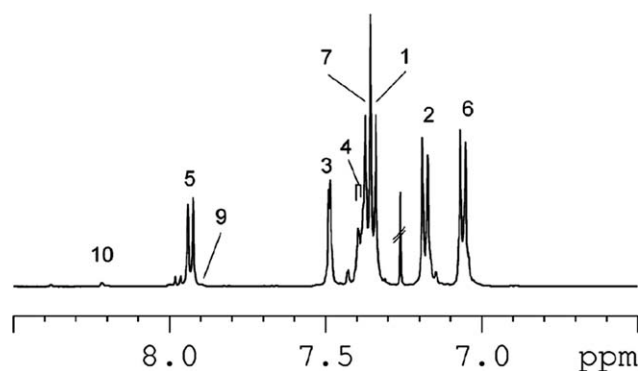
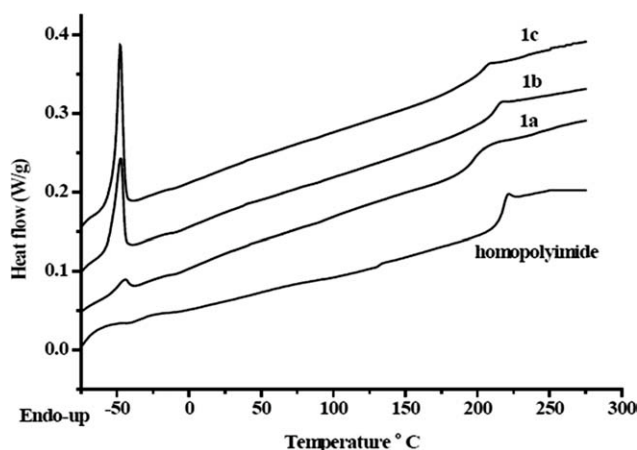


Figure 2 <sup>1</sup>H NMR spectra (signal region of aromatic protons) of **1c** (3.2 mol % DBPDMS). The atom numbering corresponds to the formula given in the Experimental Part. Solvent: CDCl<sub>3</sub>/CF<sub>3</sub>COOD (4 : 1 v/v).



**Figure 3** DSC curves of the siloxane grafted copolyimides.

siloxane grafted polymers showed  $T_g$  values of 197, 210, and 200°C depending on the siloxane loading of 10, 20, and 30 wt %, respectively. The linear segmented poly(imide siloxane)s<sup>17</sup> made from BPADA and a combination of the diamines ODA and linear aminopropyl terminated polydimethylsiloxane showed  $T_g$  values of 187, 169, and 137°C when the siloxane loading was kept to 10, 20, and 30 wt %, respectively. Whereas, the homopolyimide made from BPADA and ODA showed a  $T_g$  value of 217°C.<sup>18</sup> These findings clearly indicate that when siloxane is in the main chain it has pronounced effect on lowering the glass transition temperature of the polymers in comparison to the siloxane grafted polymers for the same siloxane loading. In case of siloxane grafted polymers, the decrease in  $T_g$  of the polyimide backbone with increasing siloxane loading is marginal whereas a sequential decrease in  $T_g$  is observed with increase in siloxane loading for the linear block-like polymers. The  $T_g$ s of the siloxane grafted copolyimides obtained from DSC are also in good agreement with the  $T_g$ s observed from DMA

measurements as shown in Table II. This interesting feature can be attributed to the fact that in the silicon grafted polyimides, the siloxane side chains contribute only slightly or not at all to the flexibility of the polyimide chain, demonstrated also by the observation of a low temperature melting transition of the siloxane chains pointing to an effective phase separation within those products. Therefore, the  $T_g$  values of the polyimide chain approach those of homopolyimide without siloxane moiety.<sup>18</sup>

### Thermal stability

The thermal stability of the polymers was investigated by dynamic TGA in nitrogen and air atmosphere. The results of TGA thermograms of the polymers recorded in nitrogen atmosphere are shown in Figure 4 and the results are summarized in Table II. As expected, compared to the 5% decomposition temperature of 526°C in nitrogen atmosphere for the homopolyimide without siloxane moiety, the siloxane grafted copolyimides show lower thermal stability. The thermal stability in nitrogen as well as in air atmosphere at 5% weight loss temperature decreases with increase in siloxane loading for the silicon grafted copolyimides. This decrease in thermal stability with increase in loading for the siloxane grafted copolyimides is also higher in comparison to the thermal stability of the linear analogues<sup>17</sup> for the same siloxane loading recorded in both nitrogen and air atmosphere. This observation can be attributed to a reduced stabilizing effect of the polyimide backbone on the stability of the PDMS segments when introduced as grafted chains.

### Flame retardancy

MCC is a small-scale flammability testing technique to screen polymer flammability prior to scale-up and it is a convenient and relatively new technique

**TABLE II**  
Thermal Properties of the Siloxane Grafted Copolyimides

Polymer	% PDMS	$T_m^a$ (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$T_g^b$ (°C)	$T_g^c$ (°C)	Ref. $T_g^d$ (°C)	$T_d^e$ (°C)	Ref. $T_d^d$ (°C)	$T_d^f$ (°C)	Ref. $T_d^g$ (°C)	Char at 800 °C in N <sub>2</sub>
Homopolyimide	0	–	–	217 <sup>18</sup>	–	–	526	–	515 <sup>17</sup>	–	45
1a	10	–45	1.1	197	200	187 <sup>17</sup>	460	480	387	432 <sup>17</sup>	51
1b	20	–47	5.6	210	222	169 <sup>17</sup>	430	467	378	410 <sup>17</sup>	43
1c	30	–48	7.6	200	218	137 <sup>h</sup>	417	455	380	401 <sup>h</sup>	37

<sup>a</sup> Side chain melting determined by DSC.

<sup>b</sup> Glass transition temperature of the main chain of siloxane grafted copolyimides determined by DSC.

<sup>c</sup> Glass transition temperature of the main chain of siloxane grafted copolyimides determined by DMA.

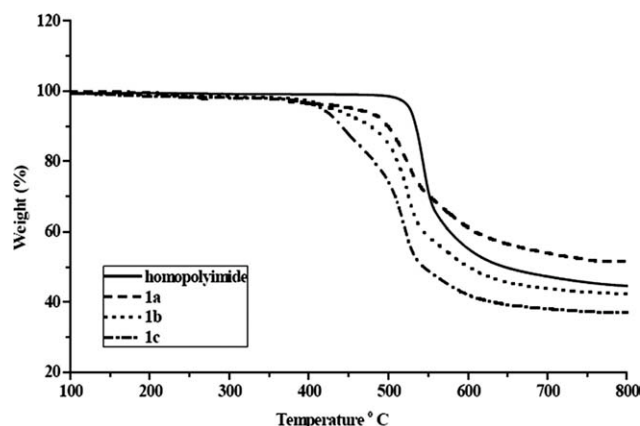
<sup>d</sup> Decomposition temperature of analogous linear poly(imide siloxane)s at 5% weight loss in nitrogen

<sup>e</sup> Decomposition temperature of the homopolyimide and siloxane grafted copolyimides at 5% weight loss in nitrogen.

<sup>f</sup> Decomposition temperature of the homopolyimide and siloxane grafted copolyimides at 5% weight loss in air.

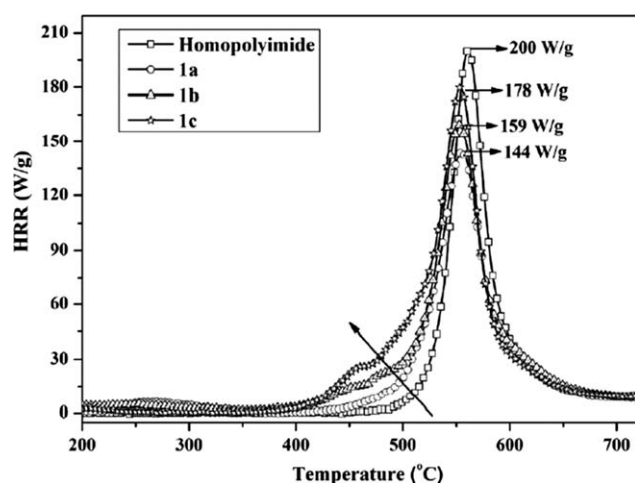
<sup>g</sup> Decomposition temperature of analogous linear poly(imide siloxane)s at 5% weight loss in air.

<sup>h</sup> The linear poly(imide siloxane) with 30% siloxane loading has been synthesized and characterized for comparison reasons in this study.



**Figure 4** TGA thermograms of siloxane grafted copolyimides in nitrogen.

which is regarded as one of the most effective methods for investigating the combustion properties of polymer materials.<sup>19–22</sup> By MCC measurements, some important parameters that reflect the combustion properties of materials can be obtained, e.g., specific heat release rate (HRR), heat release capacity (HRC), and total heat release (THR). The HRR plots obtained from the MCC of homopolyimide, **1a**, **1b**, and **1c** are shown in Figure 5 and the corresponding combustion data are presented in Table III. It is obvious that the peak HRR (pHRR) values of **1a**, **1b**, and **1c** are lower than that of homopolyimide without siloxane moiety. Comparing the pHRR value of homopolyimide of  $200 \text{ W g}^{-1}$  with those of **1a**, **1b**, and **1c** that are 144, 159, and  $178 \text{ W g}^{-1}$ , a 38, 20.5, and 11% reduction, respectively, is found. The heat release capacity (HRC) is another important parameter used to predict and evaluate the fire hazard. The HRC values obtained as sum of all peak HRR values are summarized in Table III. The results show a similar trend as well as HRR values of polymers. All



**Figure 5** Heat release rate (HRR) curves of homopolyimide and siloxane grafted copolyimides.

**TABLE III**  
Data Recorded in MCC Measurement

Polymer	pHRR ( $\text{W g}^{-1}$ )	THR ( $\text{kJ g}^{-1}$ )	$T_{mmax}$ ( $^{\circ}\text{C}$ )	HRC ( $\text{J g}^{-1} \text{K}^{-1}$ )
Homopolyimide	200	8.9	561	190
1a	144	8.5	557	139
1b	159	10.1	567	153
1c	178	11.5	555	172

HRC = heat release capacity; THR = total heat release; pHRR = peak heat release rate;  $T_{mmax}$  = temperature at maximum pyrolysis rate.

above results can be taken as indication of an improvement in flame resistance of the materials. But unfortunately, there is no reduction on total heat release (THR) for these polymers. The detailed mechanism leading to this difference is an ongoing investigation. Besides, a small increase in HRR in **1a**, **1b**, and **1c** can be observed in the temperature between 400 and 500  $^{\circ}\text{C}$ , which further increases with increasing in loading for the siloxane grafted copolyimides. These results indicate that the thermal stability of the materials decreases with increase in the loading of siloxane in siloxane grafted copolyimides, which is in accordance with the results from TGA.

### Mechanical properties

Tensile experiments were performed on dog-bone shaped specimen prepared from solution casted films. The mechanical properties of thin copolymer films are summarized in Table IV. In general, the polymer films exhibit high values for tensile strength and modulus. A tensile modulus value of 60 MPa was observed for the 10 wt % siloxane grafted copolyimide **1a** which is fully comparable to the linear

**TABLE IV**  
Mechanical Properties and Contact Angle of the Siloxane Grafted Copolyimides

Polymer	Tensile			
	Young's Modulus (MPa)	strength at break (MPa)	Elongation at break (%)	Advancing contact angle ( $^{\circ}$ )
Homopolyimide <sup>a</sup>	1080	84	13	83.3
1a	2000	60	27	105.82
Ref. PIS <sup>b</sup>	1300	59	20	99.4
1b	1300	31	23	105.6
Ref. PIS <sup>b</sup>	1230	33	25	102.4
1c	740	22	20	108.5
Ref. PIS <sup>c</sup>	970	26	74	104.2

<sup>a</sup> Values of homopolyimide taken from Ref. <sup>17</sup>.

<sup>b</sup> Values of linear poly(imide siloxane)s (PIS) with same siloxane loading taken from Ref. <sup>17</sup>.

<sup>c</sup> The linear poly(imide siloxane) with 30% siloxane loading has been synthesized and characterized for comparison reason in this study.

siloxane containing analogue<sup>17</sup> and lower than that of the homopolyimide without siloxane moiety (84 MPa).<sup>17</sup>

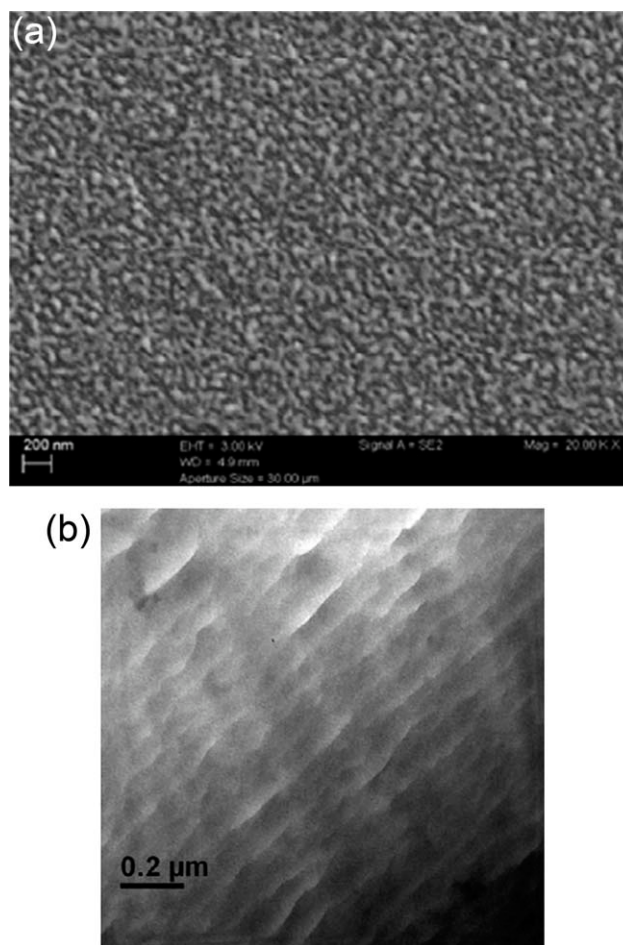
It is interesting to note that the elongation at break for the siloxane grafted copolyimides does not show any notable change with increase in siloxane loading. Hence, for the newly synthesized copolyimides containing grafted siloxane chains, the siloxane side chain does not contribute to the flexibility of the polyimide with increase in loading as observed for the linear analogues.<sup>17</sup> An elongation at break value of 27% was found for the 10 wt% siloxane grafted copolyimide **1a** which on increasing the siloxane loading to 20 and 30 wt% drops only to 23 and 20%, respectively. This finding is consistent with the observed  $T_g$  values of these polymers where the side chain siloxane group or the overall siloxane loading did not affect the glass transition temperature of the copolymers to a great extent. At the same time it is interesting to note that the modulus and tensile strength at break values of the siloxane grafted polymers **1a–1c** have a strong dependence on the total siloxane loading. These values are significantly reduced as the siloxane loading is increased and the effect is much more pronounced than for the linear analogues. This could be attributed to the reduction in polymer intra-chain interaction due to the presence of grafted siloxane moiety and as the loading increases the effect becomes more and more pronounced.

### Surface morphology

The surface morphology of the polymers was studied from the free standing films by looking at the surface to observe the distribution of the siloxane moiety in the polymer backbone. Figure 6(a) shows the representative SEM micrograph of siloxane grafted polyimide **1c**. From the micrograph a distribution of siloxane domains in the matrix phase can be seen, indicating microphase separation of the grafted siloxane as already pointed out from the DSC results. The dispersed domains are nearly spherical and the domain size is relatively small with 40–50 nm. The TEM micrograph of the skin of sample **1c** is shown in Figure 6(b). The image shows a protruded siloxane rich phase from the polyimide matrix, indicating phase segregated morphology.

### Contact angle measurement

The contact angle measurements provide information about the surface energies of the system. Contact angle (CA) is an important parameter which is often used as a measure of the hydrophobicity of a polymer surface. Contact angles were measured using water as a medium to investigate surface wett-



**Figure 6** (a) SEM micrograph of polymer **1c**. (b) TEM image of polymer **1c**.

ability. Contact angles were measured as average values over a large number of measurements on the flat free standing films and the mean of the entire values has been reported. The water contact angle for both the linear siloxane segmented analogues and siloxane grafted polymers were measured and it was found that the values are 3°–4° higher than the linear block type poly(imide siloxane)s for the same siloxane loading. The results shown in Table IV indicate that all these polymers are hydrophobic in nature with average contact angle higher than 100° with low effect of the siloxane loading.

### CONCLUSIONS

Three new polysiloxane grafted copoly(ether imide)s with siloxane loading of 10, 20, and 30 wt % have been prepared successfully and their properties have been compared with copoly(imide siloxane)s where the polysiloxane segment is incorporated into the main chain and with the homopolyimide without siloxane moiety. Several advantages of the grafted siloxanes over the polysiloxane in the main chain



have been identified. The observed melting of the siloxane graft chains indicates a strong phase separation. The glass transition temperature of the siloxane grafted copolyimides of the main chain retains in the range of 200–222°C which is close to that of the homopolyimide without siloxane moieties (217°C) while keeping a moderate thermal stability in nitrogen and air atmosphere up to at least 400°C. In comparison, the linear copoly(imide siloxane)s showed systematic decrease in  $T_g$  values with increase in siloxane loading. The flame retardance has been improved after introducing the grafted siloxane moiety in the structure of copolyimides.

Thus, with the siloxane grafted copolyimides one can design materials having better processability without affecting the glass transition temperature. Such siloxane grafted copolyimides can be of great interest for surface modifications, cable insulation and for gas separation membranes.

The authors thank P. Treppe for GPC measurements, K. Arnold for DSC and TGA measurements, R. Jurk for DMA measurements, K. Schneider for mechanical testing, M. Auf der Landwehr for SEM, and K.W. Stöckelhuber for contact angle measurements, all coworkers from IPF Dresden.

## References

1. Mittal, K. L., Ed. *Polyimides and Other High Temperature Polymers*; VSP/Brill: Leiden, The Netherlands, 2009; Vol. 5.
2. Wang, K.-L.; Liu, Y.-L.; Shih, I.-H.; Neoh, K.-G.; Kang, E.-T. *J Polym Sci A Polym Chem* 2010, 48, 5790.
3. Novák, I.; Sysel, P.; Zemek, J.; Špírková, M.; Velič, D.; Aranyosiová, M.; Florián, Š.; Pollák, V.; Kleinová, A.; Lednický, F.; Janigová, I. *Eur Polym J* 2009, 45, 57.
4. Wang, L.; Zheng, S. *Polymer* 2010, 51, 1124.
5. Hu, S.; Ren, X.; Bachman, M.; Sims, C. E.; Li, G. P.; Allbritton, N. *Anal Chem* 2002, 74, 4117.
6. Baron, A.; Rodriguez-Hernandez, J.; Ibarboure, E.; Derail, C.; Papon, E. *Int J Adhes and Adhes* 2009, 29, 1.
7. Akiyama, E.; Takamura, Y.; Nagase, Y. *Makromol Chem* 1992, 193, 2037.
8. Nagase, Y.; Mori, S.; Egawa, M.; Matsui, K. *Makromol Chem Rapid Commun* 1990, 11, 185.
9. Nagase, Y.; Mori, S.; Egawa, M.; Matsui, K. *Makromol Chem* 1990, 191, 2413.
10. Itoh, M.; Mita, I. *J Polym Sci A Polym Chem* 1994, 32, 1581.
11. Lu, S.-Y.; Hamerton, I. *Prog Polym Sci* 2002, 27, 1661.
12. Mosurkal, R.; Tucci, V.; Samuelson, L. A.; Smith, K. D.; Westmoreland, P. R.; Parmar, V. S.; Kumar, J.; Watterson, A. C. *Novel Organo-Siloxane Copolymers for Flame Retardant Applications*, ACS Symposium Series, American Chemical Society: Washington, DC, 2010; Vol. 1051, Chapter 13, p 157.
13. Zhang, S.; Horrocks, A. R. *Prog Polym Sci* 2003, 28, 1517.
14. Bourbigot, S.; Bras, M. L.; Duquesne, S.; Rochery, M. *Macromol Mater Eng* 2004, 289, 499.
15. Lv, P.; Wang, Z. Z.; Hu, Y.; Yu, M. G. *J Polym Res* 2009, 16, 81.
16. Ghosh, A.; Banerjee, S.; Komber, H.; Häußler, L.; Schneider, K.; Voit, B. *Macromol Mater Eng* 2011, 296, 391.
17. Ghosh, A.; Sen, S. K.; Dasgupta, B.; Banerjee, S.; Voit, B. *J Membr Sci* 2010, 364, 211.
18. Li, Y. S.; Wang, X. Q.; Ding, M. X.; Xu, J. P. *J Appl Polym Sci* 1996, 61, 741.
19. Hergenrother, P. M.; Thompson, C. M.; Smith, J. G.; Connell, J. W.; Hinkley, J. A.; Lyon, R. E.; Moulton, R. *Polymer* 2005, 46, 5012.
20. Wang, D. Y.; Song, Y. P.; Lin, L.; Wang, X. L.; Wang, Y. Z. *Polymer* 2011, 52, 233.
21. Wang, D. Y.; Das, A.; Costa, F. R.; Leuteritz, A.; Wang, Y. Z.; Wagenknecht, U.; Heinrich, G. *Langmuir* 2010, 26, 14162.
22. Wang, D. Y.; Leuteritz, A.; Wang, Y. Z.; Wagenknecht, U.; Heinrich, G. *Polym Degrad Stab* 2010, 95, 2474.