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New Fluorinated Poly(imide siloxane) Random and Block Copolymers with Variation of Siloxane Loading

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Several new random and block copoly(imide siloxane)s have been prepared by the solution polycondensation of commercially available 4,4′-oxydianiline (ODA) and amino-propyl terminated polydimethylsiloxane (APPS) with 4,4′-(hexafluoro-isopropylidene)diphthalic anhydride (6FDA). The siloxane loading was kept to 10, 20, 30, 40 and 50 wt% in the copolymers. The random copolymers were prepared by a one pot solution imidization technique, and two pot solution imidization technique was adopted for the synthesis of the block copolymers. The diamine ODA and the dianhydride 6FDA composed the hard block segment, while APPS and 6FDA composed the soft block segment. The hard block length was kept constant while the soft block lengths were varied by varying the siloxane loading. Accordingly, block copoly(imide siloxane)s were prepared on increasing the soft block lengths (DP) from 3 to 6, 10, 18 and 36 for fixed hard block length of 22. The resulting polymers have been well characterized by IR, NMR and GPC techniques. Thermal and mechanical properties of the random and block copolymers were compared with the already reported homopolyimide without siloxane moiety.

Keywords: Fluorinated polyimides, poly(imide siloxane), glass transition temperatures, thermal properties, mechanical properties

1 Introduction

High-performance polymers such as polyimides are well known for their outstanding properties such as excellent thermal and thermo-oxidative stability, solvent resistance, mechanical and electrical properties (1, 2). Despite such attractive properties, this class of polymers suffers from insolubility and intractability, which cause difficulties in both synthesis and processing. Much effort has been spent on synthesizing tractable, soluble and/or melt processable variations by reducing polymer chain–chain interactions, chain packing or charge-transfer electronic polarization interactions.

Fluorinated polyimides (3, 4) have received special attention because of their many interesting properties such as low dielectric constant, low moisture absorption, high thermal stability and chemical resistance due to the high electronegativity of fluorine atoms and low electron polarizability of C-F bonds (5–7). Incorporation of fluorine also enhances the solubility (8). Hexafluoroisopropylidene (6F) or pendent trifluoromethyl groups (9–13) in polyimides serve to increase the free volume of the polyimides, thereby improving various properties like solubility, electrical insulating properties and gas permeability without forfeiture of thermal stability. These groups tend to decrease water absorption, crystallinity and color, while they increase flame resistance, environmental stability and optical transparency. Solubilization of the polyimides has also been attempted by several means, such as the introduction of flexible siloxane segment. Incorporation of the flexible siloxane segment into the polyimide backbone imparts enhanced solubility, reduces water uptake, increases gas permeability and allows for good thermal stability. Such interesting properties make siloxane-modified polyimides useful materials for aerospace applications and electronic devices (14–17).

In our previous studies, we have reported that the glass-transition temperature (T_g) can be controlled by variation of siloxane loading in random copoly(imide siloxane)s (14, 15). We also reported for block copoly(imide siloxane)s that simply by varying the hard and soft block length keeping the siloxane loading constant, T_g can be also be excellently adjusted (16). Thus, we could demonstrate that with perfectly alternating segmented copolymers of various block lengths, it is possible to control the T_g and modulus of the block copoly(imide siloxane)s.

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In the present study, we report on the successful one pot synthesis of random copolymers by reacting commercially available 4,4′-(hexafluoro-isopropylidene)diphthalic anhydride (6FDA), 4,4′-oxydianiline (ODA) and amino-propyl terminated polydimethylsiloxane (APPS) as a comonomer with variation of siloxane loading of 10, 20, 30, 40 and 50 wt%, respectively. The random copolymers are named as.1a, 2a, 3a, 4a, 5a. The random copolymer 2a has already been reported (17). In our previous report on block copolymers, we have varied both the hard and soft block lengths keeping a fixed level of siloxane loading (16). In this study, we varied the siloxane loading in the block copolymers from 10 to 50 wt% with an interval of 10 wt% similar to the random copolymers. For an overall stoichiometric balanced reaction, with a fixed hard block DP of 22, the soft block DP's varied from 3 to 6, 10, 18 and 36, respectively, in accordance with a siloxane loading of 10, 20, 30, 40 and 50 wt% in the final block copolymers named as 1b, 2b, 3b, 4b and 5b. The resulting polymers have been well characterized by spectroscopic, thermal and mechanical techniques. The properties of the block copolymers are compared with the analogous random copolymers and with the already reported homopolyimide prepared without APPS (18).

2 Experimental

2.1 General Consideration

Carbon, hydrogen and nitrogen of the compounds were analyzed by pyrolysis method. ^{1}H-NMR was recorded on a Bruker 500 MHz instrument (Switzerland) using $CDCl_3$ as solvent. IR spectra of the polymer films were recorded with a Netzsch 870 FTIR spectrophotometer instrument (Germany). DSC measurements were made on a DSC Q 1000 of TA Instruments (USA) 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 behaviour of these polymers was measured using a Perkin-Elmer (Pyris Diamond) instrument (USA) at a heating rate of 10°C/min under air. Mechanical properties such as tensile strength and elongation at break of the thin polymer films (30 × 0.1 mm) were measured at room temperature on a Hounsfield H10KS - 0547 instrument (UK) under strain rate of 5%/min of the sample length. Gel permeation chromatography was performed in THF with a PL MIXED-C column (pore size 5 μm) from Polymer Laboratories at a flow rate of 1.0 mL min^{-1} with linear polystyrene as a standard, using MALLS Detector from Wyatt Technologies. HPLC-Pump 64 from Knauer was used for this investigation. 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. The samples 1b, 2b and 3b were not soluble in THF up to 50°C and hence, the GPC of these samples were carried out in DMAc + 3g/l LiCL as solvent.

2.2 Starting Materials

6FDA was purchased from Aldrich (USA) and was heated at 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.

Aminopropyl terminated polydimethylsiloxane (APPS) of average molecular weight 865 g/mol was purchased from Gelest Inc., USA. 1, 2-Dichlorobenzene (ODCB) (E. Merck, India) was used as received. Methanol was purchased from Ranbaxy Fine Chem Ltd, India.

2.3 Polymerization

2.3.1. *Preparation of Random Copolymers*

The polymerization reactions were conducted by the reaction of 6FDA and two different diamines in a random fashion. The reactions were conducted under constant flow of nitrogen. A representative polymerization procedure for poly(imide siloxane) 1a is as follows.

A 50 mL 3 necked round-bottomed flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with 1.272 g (2.8639 mmol) 6FDA, 0.52 g (2.6319 mmol) of ODA, 0.2006 g (0.2319 mmol) APPS and 20 mL of 1,2-dichorobenzene. The reaction was carried out under constant stirring and nitrogen flow. The temperature of the reaction medium was raised slowly from room temperature to 180°C. The reaction was continued for 6 h at 180°C. During the course of reaction, the solution was observed to turn viscous. The resulting viscous polymeric solution was cooled to room temperature and was precipitated from 500 mL methanol. The fibrous product obtained was dried and dissolved in 20 mL dichloromethane and re-precipitated from methanol. The fibrous product was dried at 120°C for 5 h under vacuum and used for further analysis. A weighed quantity of polymer was dissolved in a measured amount of dichloromethane (15 wt%) and was poured in flat bottom Petri dishes to obtain polymer films. The Petri dishes were covered and the solvent was allowed to evaporate at a controlled rate at 30°C overnight. The Petri dishes were then kept in a vacuum oven and the temperature of the oven was slowly raised to 120°C and kept under continuous vacuum for 5-6 h to remove any trace of solvent. Finally, the Petri dishes were placed in boiling water to remove the films.

2.3.2. *Preparation of Block Copolymers*

2.3.2.1. *Preparation of soft block segment (S).* The anhydride terminated soft blocks were prepared by the reaction of 6FDA with APPS. The exact feed ratios are given in Table 1. A three-necked 50 mL round bottom flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with 0.2043 g (0.46 mmol) 6FDA and 6 mL ODCB. The temperature of the reaction mixture was raised to 60°C to dissolve the 6FDA in ODCB and then 0.2006 g (0.2320 mmol) APPS

Table 1. Feed ratio for preparation of block copolymers, calculated r values, degrees of polymerization, hard and soft block weight fraction and calculated siloxane loading

	Hard block feed composition			*Soft block feed composition*								
Polymer	*6FDA (g/mmol)*	*ODA (g/mmol)*	*r/DP$_n$ (K)*	*6FDA (g/mmol)*	*APPS (g/mmol)*	*r/DP$_n$(L)*	*Hard block quantity (g)*	*Soft block quantity (g)*	*Total polymer (g)*	*Hard block weight fraction* (%)	*Soft block weight fraction* (%)	*Siloxane loading (%)*
1b	1.0679/2.4040	0.5269/2.632	0.9133/22.08	0.2043/0.4600	0.2006/0.2320	0.5043/3.03	1.5425	0.3965	1.94	79.55	20.45	10.05
2b	0.8765/1.9730	0.4324/2.16	0.9135/22.13	0.2892/0.651	0.4017/0.464	0.7133/5.97	1.2379	0.6742	1.91	64.74	35.26	20.40
3b	0.6868/1.546	0.3388/1.692	0.9135/22.14	0.3735/0.841	0.6007/0.695	0.8260/10.49	0.9699	0.9492	1.92	50.54	49.46	30.39
4b	0.4960/1.117	0.2447/1.222	0.9134/22.09	0.4583/1.032	0.8009/0.926	0.8974/18.49	0.7005	1.2259	1.93	36.36	63.64	40.37
5b	0.3052/0.687	0.1506/0.752	0.9130/22.01	0.5431/1.2230	1.000/1.157	0.9465/36.39	0.4311	1.5014	1.93	22.31	77.69	50.25

r = moles of 6FDA/moles of ODA (for hard block) and moles of APPS/moles of 6FDA (for soft block); $DP_n = (1 + r)/(1 - r)$.

in 2 mL of ODCB were added. The small glass vial in which APPS was weighed was washed twice by 2 mL ODCB for efficient transfer of APPS. The reaction temperature was raised to 150°C, the reaction was conducted for 2 h and this soft block was used for the preparation of block copolymer of 1b. The other soft blocks were also prepared in a similar way but taking different amounts of 6FDA and APPS.

2.3.2.2. *Preparation of hard block segment (H).* The amine terminated hard block was prepared by the reaction of the desired quantity (Table 1) of 6FDA with ODA. In a typical synthesis, a three-necked 50 mL round bottom flask equipped with nitrogen inlet, a magnetic stirrer and Dean-Stark trap fitted with a condenser was charged with 1.068 g (2.404 mmol) 6FDA, 0.5269 g (2.632 mmol) ODA and 10 mL ODCB. The temperature of the reaction mixture was raised slowly to 150°C and the reaction was conducted for 2 h; this hard block was used for the preparation of block copolymer 1b.

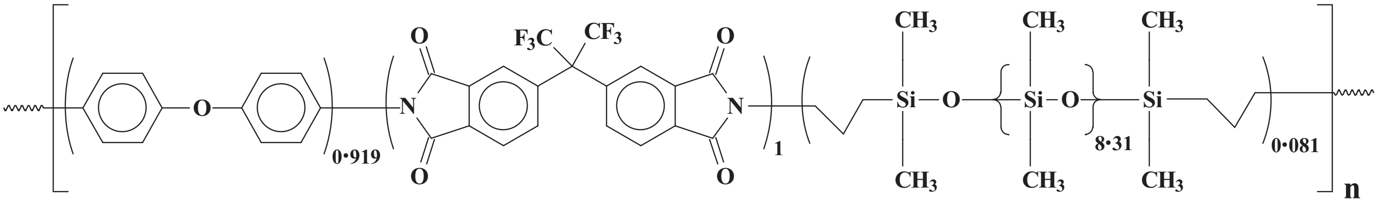
2.3.2.3. *Preparation of the block co-polymers.* After 2 h of heating the hard and soft block segments separately, the soft block was transferred to the hard block. The flask was washed with some additional amount of ODCB which was added to the final reaction mixture to ensure complete transfer of soft block segment to the hard block containing flask. The reaction temperature was raised to 180°C and the reaction was continued for another 4 h at this temperature. During the course of reaction, water formed due to imidization was removed azeotropically by ODCB and accordingly fresh solvent was added to makeup for the solvent loss to maintain the solid content in the reaction mixture roughly at about 10 wt%. The reaction temperature was brought down to room temperature and the polymer solution was precipitated in 500 mL methanol. The fibrous product obtained was dried and dissolved in 20 mL dichloromethane and re-precipitated from methanol. The products were dried at 120°C for 5 h under vacuum and were used for further analysis. Thin films of the block copolymers were prepared by the same protocol as discussed for the random copolymers.

2.3.3. *Preparation of Soft Block Segments for NMR Analysis*

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

Poly(imide siloxane) 1a

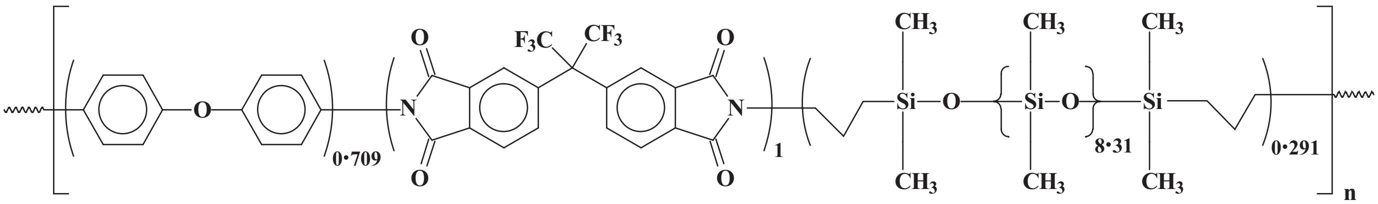
Batch size: 6FDA, 1.2723 g (2.863 mmol); ODA 0.5269 g (2.631 mmol); APPS, 0.2006 g (0.2319 mmol); ODCB, 20 mL.



Analytical calculation for $(C_{32.1842}H_{19.3346}O_{5.6731}F_6N_2Si_{0.8351})_n$ (662.296 gmol^{-1})$_n$: C, 58.36%; H, 2.94%; N, 4.23%; Found: C,58.43 %; H, 2.98%; N, 4.54%. **IR (KBr) (cm^{-1}):** 2960 (-CH_3 group present in APPS); 1783 and 1728 (asymmetric and symmetric –CO- stretch); 1623 (C=C ring stretching band); 1502 (band due to C-F absorption); 1376 (C-N stretch); 1148 and 1094 (Si-O-Si stretching); 801 (Si-C). **^{1}H-NMR ($CDCl_3$): δ (ppm)** 8.05-7.19 (14.93 H), 3.68 (s, 0.32H, -CH_2–N<), 1.63 (s, 0.29 H, -CH_2-), 0.91-0.51 (m 0.29 H, -CH_2-Si), 0.13–0.02 (m, 4.40 H, Si-CH_3)

Poly(imide siloxane) 3a

Batch size: 6FDA, 1.060 g (2.3868 mmol); ODA 0.3388 g (1.692 mmol); APPS, 0.6007 g (0.6945 mmol); ODCB, 20 mL.

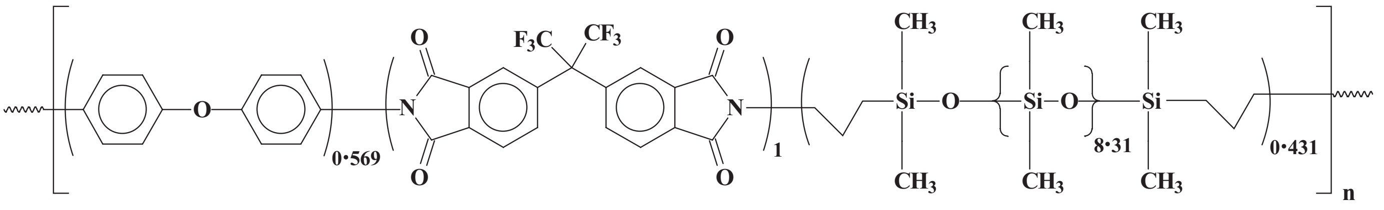


Analytical calculation for $(C_{35.2544}H_{33.1652}O_{7.4182}F_6N_2Si_{3.0002})_n$ (801.852 gmol^{-1})$_n$: C, 52.80%; H, 4.17%; N, 3.49%; Found: C,52.98 %; H, 4.29%; N, 3.56%. **IR (KBr) (cm^{-1}):** 2961 (-CH_3 group presentin APPS); 1781 and 1726 (asymmetric and symmetric –CO- stretch); 1624 (C=C ring stretching band); 1503 (band due to C-F absorption); 1380 (C-N stretch); 1148 and 1094 (Si-O-Si stretching); 799 (Si-C). **^{1}H-NMR ($CDCl_3$): δ (ppm)** 8.05-7.19 (13.18 H), 3.68

(s, 1.16H, -CH_2–N<), 1.69 (s, 1.03 H, -CH_2-), 1.25-0.56 (m 1.03 H, -CH_2-Si), 0.16-0.06 (m, 19.58 H, Si-CH_3)

Poly(imide siloxane)4a

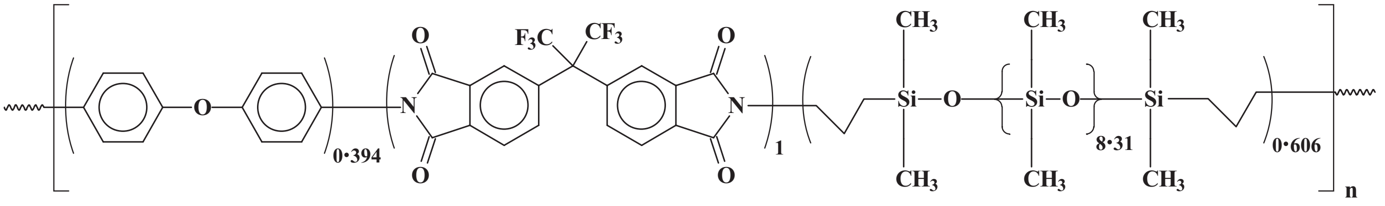
Batch size: 6FDA, 0.9543 g (2.1482 mmol); ODA 0.2447 g (1.2223 mmol); APPS, 0.8009 g (0.9258 mmol); ODCB, 20 mL.



Analytical calculation for $(C_{37.3012}H_{42.3856}O_{8.5816}F_6N_2\text{-}Si_{4.4436})_n$ $(894.890\ \text{gmol}^{-1})_n$: C, 50.06%; H, 4.77%; N, 3.13%; Found: C,50.23 %; H, 4.83%; N, 3.43%. **IR (KBr) (cm^{-1}):** 2960 (-CH_3group presentin APPS); 1780 and 1727 (asymmetric and symmetric –CO- stretch); 1622 (C=C ring stretching band); 1502 (band due to C-F absorption); 1383 (C-N stretch); 1147 and 1093 (Si-O-Si stretching); 798 (Si-C). **^{1}H-NMR ($CDCl_3$):** ***δ* (ppm)** 8.06-7.19 (13.18 H), 3.68 (s, 1.72H, -CH_2–N<), 1.69 (s, 1.34 H, -CH_2-), 1.25-0.56 (m 1.54 H, -CH_2-Si), 0.16- 0.06 (m, 31.76 H, Si-CH_3)

Poly(imide siloxane) 5a

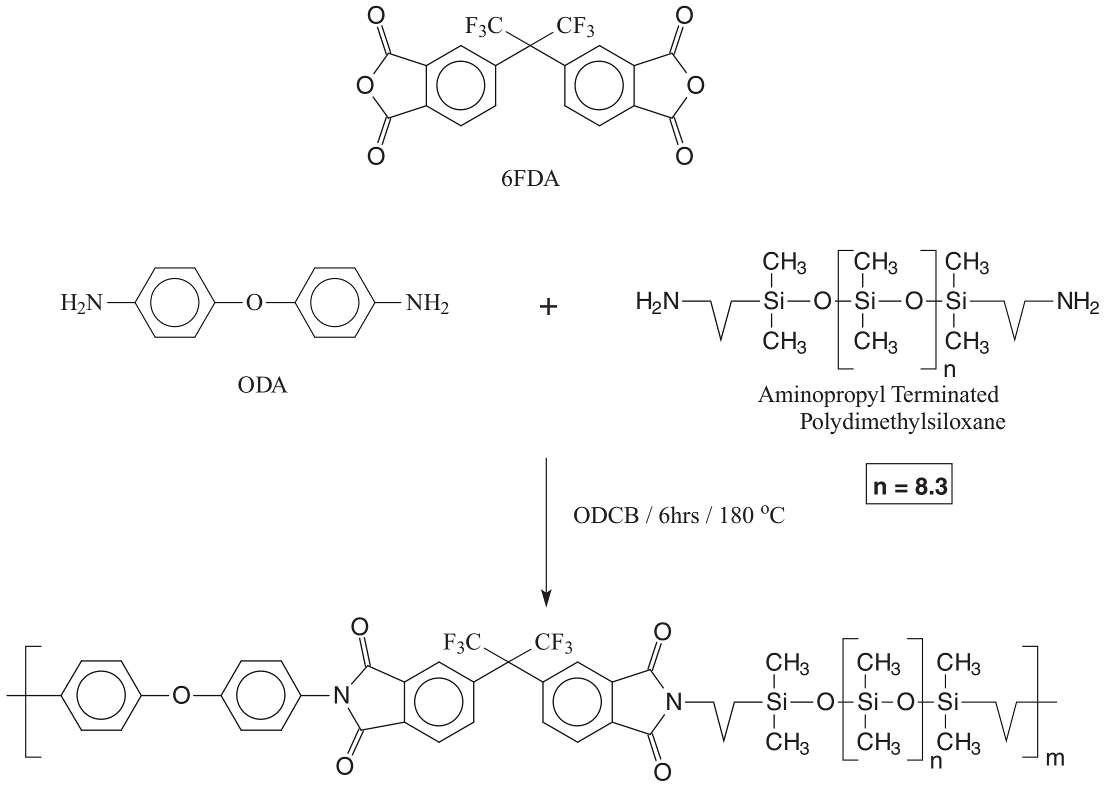
Batch size: 6FDA, 0.8483 g (1.9096 mmol); ODA 0.1506 g (0.7523 mmol); APPS, 1.0000 g (1.1572 mmol); ODCB, 20 mL.



Analytical calculation for $(C_{39.8597}H_{53.9116}O_{10.0358}F_6N_2\text{-}Si_{6.2478})_n$ $(1011.187\ \text{gmol}^{-1})_n$: C, 55.56%; H, 3.56%; N, 3.85%; Found: C,55.83 %; H, 3.43%; N, 3.98%. **IR (KBr) (cm^{-1}):** 2962 (-CH_3group presentin APPS); 1784 and 1731 (asymmetric and symmetric –CO- stretch); 1624 (C=C ring stretching band); 1504 (band due to C-F absorption); 1378 (C-N stretch); 1157 and 1093 (Si-O-Si stretching); 802 (Si-C). **^{1}H-NMR ($CDCl_3$):** ***δ* (ppm)** 8.06-7.19 (10.70 H), 3.72 (s, 2.42H, -CH_2–N<), 1.69 (s, 2.18 H, -CH_2-), 1.34-0.57 (m 2.20 H, -CH_2-Si), 0.16- 0.05 (m, 41.37 H, Si-CH_3)

3 Results and Discussion

The reaction scheme and polymer structures are shown in Figure 1 for the random copolymers and in Figure 2 for the block copolymers. In Figure 2, the soft block lengths of five different block copolymers synthesized are denoted by 'L' and the hard block length is denoted by 'K', respectively. The values K and L were calculated from the stoichiometric imbalance used in the feed composition (Table 1). The polymers were prepared by conventional two pot solution imidization method. In the present synthesis 1,2- dichlorobenzene (ODCB) was used as the solvent with a solid content of about 10 wt%. The soft blocks of different degrees of polymerization (DP) and the hard block of fixed DP were prepared separately in two different flasks. The number average degree of polymerization DP_n of the blocks was calculated from the equation, $DP_n = (1 + r)/(1 + r - 2rp)$, where p is the extent of reaction and r is the stoichiometric imbalance. The r value is defined as the total number of amine/anhydride (hard block) or anhydride/amine (soft block) functional groups initially present. The value of r is always less than 1. For the reaction between highly reactive species like amines and anhydrides the extent of reaction can be considered as 1. In such a condition $DP_n = (1 + r)/(1 – r)$ and this equation was used to calculate the degree of polymerization. The reactions were designed in such a way that the DP_n for hard blocks was the same in all the five different copolymers prepared while the soft block lengths were varied. The soft blocks were prepared by dissolving weighed amount of 6FDA in ODCB at 60°C and APPS was added onto it in a defined stoichiometric amount. The temperature of the reaction mixture was raised to 150°C and maintained for 2 h. Similarly, the hard block was prepared by reacting ODA with a stoichiometric amount of 6FDA at 150°C for 2 h. The final polymers were prepared by transferring the anhydride rich soft blocks to the amine rich hard block; the polymerization temperature was raised to 180°C and continued for another 4 h. After this period the polymers were isolated by precipitation from excess amount of methanol, the precipitates were dried and were used for further analyses. GPC molecular weights of the poly(imide siloxane)s shown in Table 2 indicate formation of very high molar mass products with M_w values up to 250,000 g/mol.



Siloxane loading	10 wt%	20 wt%	30 wt%	40 wt%	50 wt%
Polymer code	1a	2a	3a	4a	5a

Fig. 1. Reaction scheme and structures of random poly(imide siloxane)s.

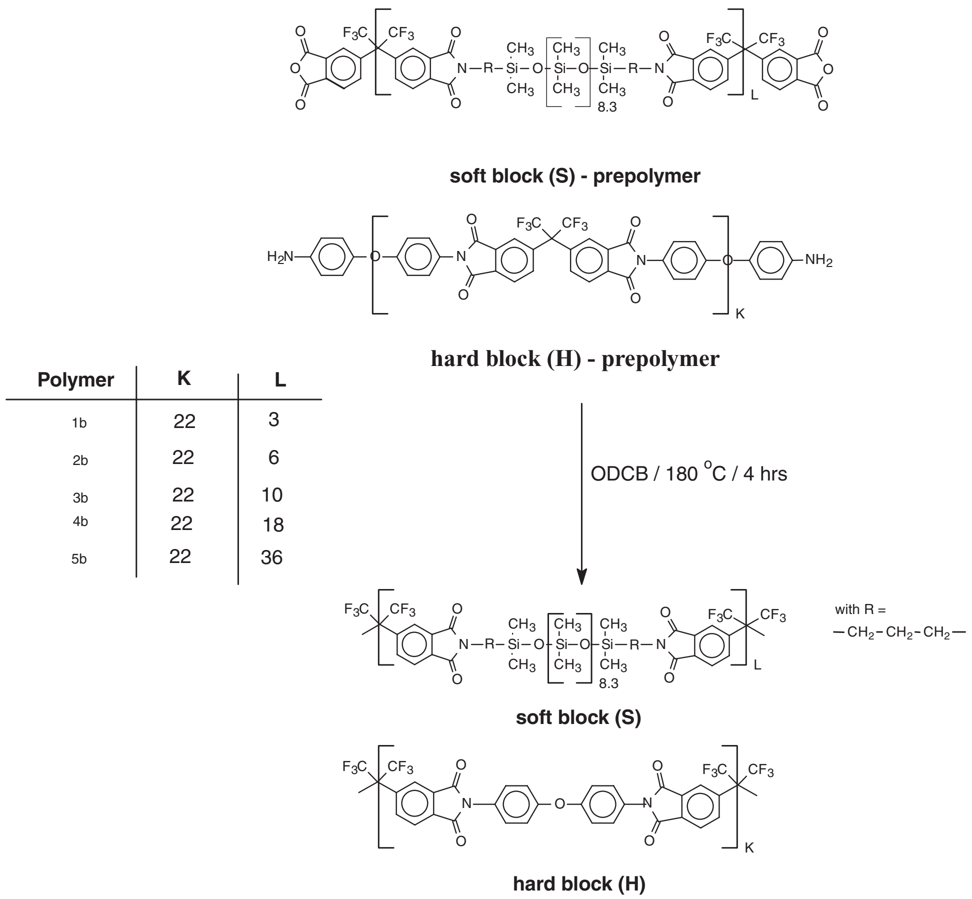
3.1 Polymer Solubility

The solubility of the resulting poly(imide siloxane)s was investigated in different organic solvents. The results are presented in Table 2. All 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), tetrahydrofuran (THF), chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2), and were observed to be insoluble in dimethyl sulphoxide and acetone. All block copolymers exhibited very good solubility in common organic solvents except 1b, 2b and 3b which were not soluble in THF upto 50°C and hence, GPC measurements were performed in DMAc + 3g/l LiCL as solvent.

Table 2. GPC molecular weights and solubility of the random and block copolymers

Polymer	M_w *(g/mol)*	*PDI*	*NMP*	*DMF*	*DMAc*	*DMSO*	*THF*	$CHCl_3$	CH_2Cl_2	*Acetone*
1a	187300	1.52	+	+	+	−	+	+	+	−
3a	74300	1.13	+	+	+	−	+	+	+	−
4a	82500	1.26	+	+	+	−	+	+	+	−
5a	253900	1.56	+	+	+	−	+	+	+	−
1b**	86000	2.71	+	+	+	−	−	+	+	−
2b**	59300	2.60	+	+	+	−	−	+	+	−
3b**	70100	2.94	+	+	+	−	−	+	+	−
4b	91600	1.27	+	+	+	−	+	+	+	−
5b	114300	1.26	+	+	+	−	+	+	+	−

M_w = weight average molecular weight by GPC; PDI = polydispersity index; +soluble at room temperature; −, insoluble at reflux.
**solvent DMAc + 3g/l LiCL.



Polymer	K	L
1b	22	3
2b	22	6
3b	22	10
4b	22	18
5b	22	36

Fig. 2. Reaction scheme and structures of block copoly(imide siloxane)s.

3.2 Spectroscopy

The formation of poly(imide siloxane) copolymers was confirmed by FTIR. The FTIR spectra of the polyimide films show absorption bands at about 1780 cm^{-1} (C=O asymmetric stretching) and 1720 cm^{-1} (C=O symmetric stretching), corresponding to the imide bands (9). The strong absorption band at 2961 cm^{-1} corresponds to the C-H stretching of the methyl groups attached to silicon in APPS. The strong absorption bands at 1080, 1020 cm^{-1} (Si-O-Si stretching), and 800 cm^{-1} (Si-C stretching) are characteristic for the siloxane group.

A representative ^{1}H-NMR spectrum of 3a is given in Figure 3. Table 3 represents the number of aromatic and aliphatic protons calculated from the structures of random poly(imide siloxane)s, comparing those expected from the feed ratio of the components 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 lower than that calculated from the expected gross molecular structure. It is observed that though the poly(imide siloxane)s have been prepared with the view of incorporating 10, 30, 40 and 50 wt% siloxane loading, actual incorporation is found to be a few percent lower in each case (roughly 8, 17, 28, 37, and 46%). The reason for the somewhat lower siloxane incorporation has already been discussed in detail in our previous article (14(a)).

Table 3. Calculated number of aromatic and aliphatic protons from gross molecular structure from feed ratio vs. the protons found from NMR for random copolymers

Polymer	*C-aro*	*C-ali*	*F-aro*	*F-ali*	*C-ali/ aro*	*F-ali/ aro*	*Actual siloxane (%)*
1a	13.35	5.98	14.93	5.79	0.448	0.388	8.6
2a[15]	12.58	13.07	13.35	12.16	1.038	0.910	17.5
3a	11.67	21.49	13.09	22. 81	1.841	1.742	28.4
4a	10.55	31.83	13.18	36.37	3.016	2.759	36.6
5a	9.152	44.76	10.70	48.17	4.89	4.50	46.0

Where,

C-aro = Number of aromatic protons calculated from polymer structure.
C-ali = Number of aliphatic protons calculated from polymer structure.
C (ali/aro) = Ratio of aliphatic/aromatic protons from polymer repeat unit structure.

Similarly,

F (ali/aro) = ratio of aliphatic/aromatic protons found from integrated peaks ^{1}H-NMR.
Siloxane incorporation (%) = wt% of siloxane incorporation attempted × [F(ali/aro)/C(ali/aro)].

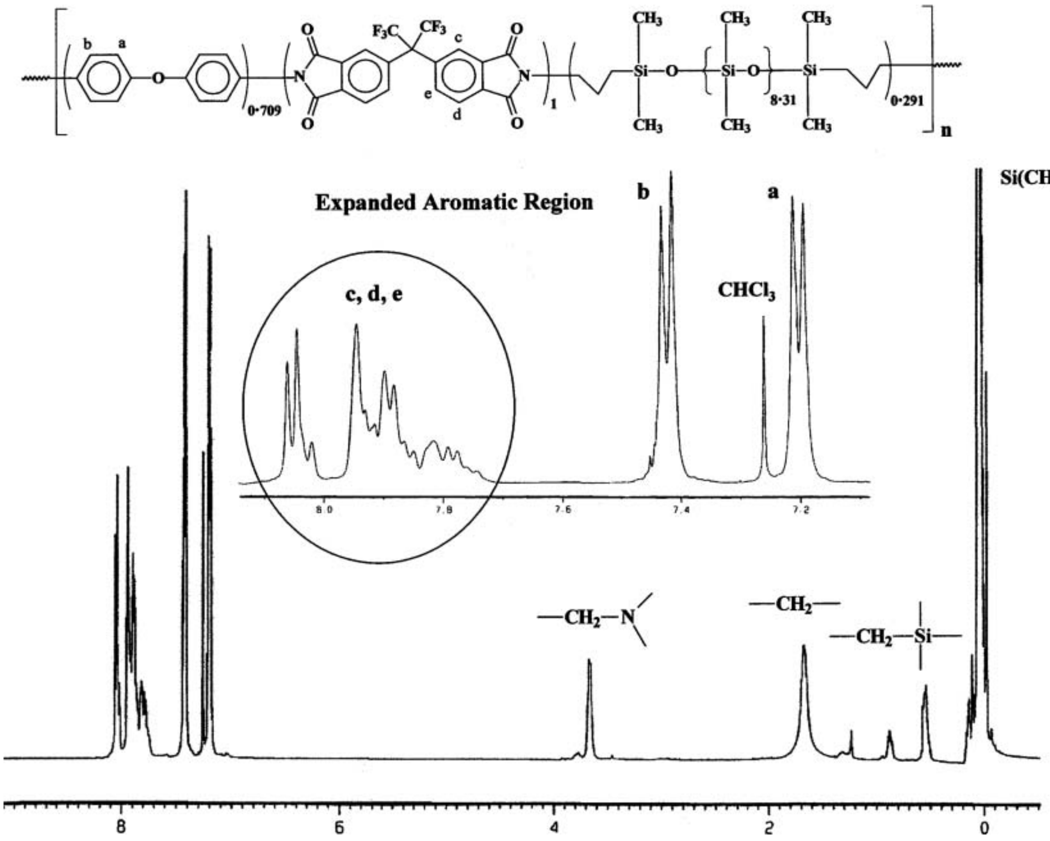


Fig. 3. ^{1}H-NMR spectra of random copoly(imide siloxane)s 3a.

It was not possible to calculate the exact block lengths that were generated in the polymers after the end of the final polymerization in a satisfactory accuracy based on NMR signal integrals. Therefore, to get an idea on block lengths, several soft blocks were prepared under similar conditions as the final polymer was prepared. According to the above mentioned equation, DP was calculated from r values which were determined from appropriate ^{1}H-NMR signal integrals. However, with increasing DP, the integration of the decreasing end group signals becomes more inaccurate. Therefore, this method only should be applied for the samples with smaller block lengths (16). Nevertheless, we can state that we do not expect from our findings, a large deviation in the block length of the soft blocks from that calculated by from stoichiometry having a variation between 3 to 36 repeating units within the siloxane part.

3.3 Glass Transition Temperature vs. Polymer Structure

The final random and block copoly(imide siloxane)s exhibited no crystallization or melting transition in DSC measurements. These polymers showed glass transition temperatures, which indicate amorphous or glassy morphology. DSC curves of the random and block polymers are shown in Figure 4. The glass transition temperature values are summarized in Table 4. A decrease in glass transition temperature is observed for random copolymers with increase in the siloxane loading in the polymer backbone (14, 15). For the block copolymers, the hard block T_g's for all the block copolymers were in the range of 240–245°C due to the constant hard block lengths. At very high level of siloxane loading, the T_g corresponding to the hard block

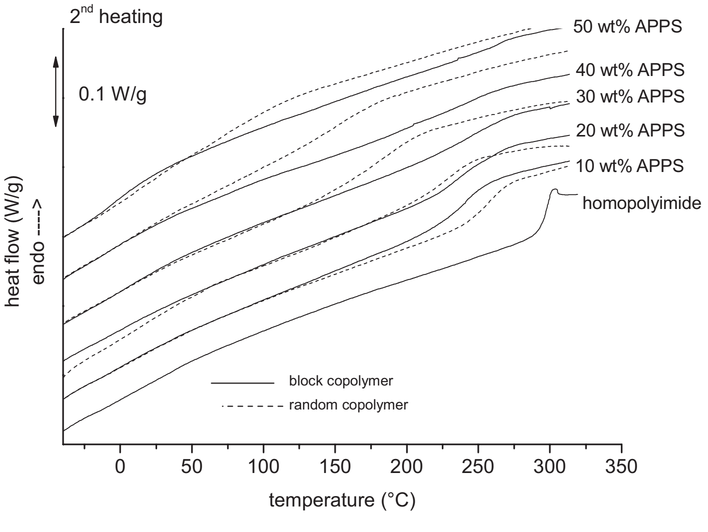


Fig. 4. Comparison of glass transition temperature of random and block copolymers.

Table 4. Thermal properties of the random and block poly(imide siloxane)

Polymer	*DSC T_g(°C)*	*Temp. at 5% weight loss (°C) in air*	*Residue at 700°C in air from TGA*
Homopolyimide	297(285.6)$^{(19)}$	515$^{(17)}$	0
1a	257	435	6.3
2a$^{(17)}$	228	419	12.8
3a	182	401	20.8
4a	157	369	26.2
5a	90	365	33.9
1b	240	460	6.2
2b	244	423	12.6
3b	245 (14)*	418	21.1
4b	242 (16)*	416	26.5
5b	240 (3)*	413	33.5

* T_g observed at low temperature.

becomes less pronounced as the weight fraction (Table 1) of the hard block decreases. For the block copolymers with higher siloxane loading of 30, 40 and 50 wt% another thermal transition was also observed in the low temperature region. Weak transitions at 14°C and 16°C were observed along with the hard block T_g for the block copolymers with siloxane loading of 30 wt% and 40 wt%, respectively. Interestingly, with a further increase in siloxane loading to 50 wt%, a pronounced thermal transition was observed at 3°C, which was attributed to the $T_g$of the soft block. It looks like the high soft block length of 36 in 5b with a total very high weight fraction of the soft block leads to microphase segregation of the soft block that resulted in a pronounced T_g in the low temperature region. However, this assumption needs further investigation to be confirmed.

3.4 Thermal Stability

The thermal stability of the copolymers was evaluated by TGA. The thermal properties of the polymers are summarized in Table 4. In order to study the suitability of the poly(imide siloxane)s for practical applications, TGA was studied in air atmosphere. The 5% weight loss temperature of these polymers is up to 435°C for the random copolymers and 460°C for the block copolymers indicating good thermal stability. The relatively higher thermal stability of the block copolymers is attributed to the formation of greater structural regularity in comparison to the random copolymers. The thermal stability is affected by incorporation of siloxane components. As the siloxane loading is increased from 10 to 50 wt% the thermal stability decreases and this decrease is more pronounced in case of random copolymers compared to that of block copolymers. All the siloxane containing polymers showed high residues at 600°C under air atmosphere. The relatively low thermal stability of these siloxane containing polymers can be attributed due to the presence of weak aminopropyl silane linkers in the polymer (20).

3.5 Mechanical Properties

The mechanical properties of thin random and block copoly(imide siloxane) films are shown in Table 5. In general, the mechanical properties of the poly (imide siloxane) films were excellent. These poly(imide siloxane)s showed a dependency of the elongation at break on the siloxane loading. Increase in siloxane loading led to higher elongation at break values and to lower tensile strength at break and modulus values compared to the analogous homopolymer (6FDA-ODA) without siloxane moiety (18). Compared to the random copolymers, the block copolymers with the same siloxane incorporation showed lower elongation at break with higher tensile strength. This change in behavior of the block copoly(imide siloxane)s is due to the very high hard block length having 22 repeating units which shows higher tensile strength but lower elongation at break. A dramatic rise in the elongation at break was observed for block copolymer with increase in siloxane loading from 40 wt% to 50 wt%. This rise is attributed to the strong

Table 5. Mechanical, water absorption and dielectric behaviour of random and block poly(imide siloxane)s

Polymer	*Tensile strength (MPa)*	*Elongation at break (%)*	*Young's Modulus (GPa)*	*Water absorption after 72 h (%)*	*Dielectric constant at 1 MHz*
Homopolyimide	78.45[18]	2.9[18]	—	2.31[21]	2.78[18]*
1a	61	4	2.30	1.00	2.69
2a[17]	53	24	1.11	0.88	2.58
3a	46	45	0.95	0.67	2.47
4a	18	90	0.80	0.56	2.38
5a	17	120	0.28	0.48	2.36
1b	63	5	2.39	1.02	2.68
2b	57	10	1.61	0.86	2.56
3b	44	13	1.23	0.65	2.49
4b	25	22	0.82	0.58	2.42
5b	15	84	0.38	0.49	2.37

* Value taken from reference [18] measured at 1 KHz.

increase in soft block length from 18 to 36 in 5b with in total a very high weight fraction of the soft block (Table 1). In summary, in comparison to the homopolyimide without siloxane moiety (18), the random and block copolymers showed lower tensile stress and higher elongation at break.

3.6 Water Absorption and Dielectric Properties

Water absorption of the poly(imide siloxane) were measured by immersing rectangular pieces of vacuum dried samples (30 × 10 mm) in double distilled water after taking their initial weight at room temperature. The final weight was taken after 72 h and the percent water absorption was calculated. Table 5 shows that the water uptake values as low as 0.48 wt% in case of the polymer 5a. The water absorption values are much lower than that observed in case of siloxane free homopolyimide (21). Reduction in water uptake of these polymers is possibly due to the contribution both from fluorine as well as siloxane units into the backbone of the polyimides, similarly as due to the same reason the dielectric constant is also observed to decrease compared with increase in incorporation of siloxane loading in the polymer backbone as can be seen from Table 5. No dramatic difference has been observed in the water absorption and dielectric constant values with the same siloxane loading for the random and blocks copolymers.

4 Conclusions

Five new random and block copoly(imide siloxane)s were prepared by reacting 6FDA as dianhydride with two different diamines, ODA and APPS. The random copolymers were prepared by one pot, and block copolymers were prepared by two pot solution imidization technique. Products with very high molar masses of up to 250,000 g/mol (M_w) have been achieved. It was not possible to calculate the exact block length of the block copolymers in a satisfactory accuracy based on NMR signal integrals, but it was attempted to keep the hard block constant with about 22 repeating units and to vary the length of the soft block from about 3 to 36 repeating units, adjusting the stoichiometric imbalance in the feed composition.

In the case of random copolymers, a continuous decrease of glass transition temperature was observed with increase in siloxane loading. DSC results for the block copolymers show a T_g for the hard block in the range of 240–245°C which allowed to retain a much better heat stability for the block copolymers compared to the random copolymers. With an increase in the soft block length, a T_g was also observed in the low temperature range indicating phase separation. The formation of different block lengths has also consequences on the mechanical properties of the random and block copolymers. With an increase in the siloxane loading, Young's modulus shows a decrease, however this decrease was lower in the case of block copolymers possibly due to the greater structural regularity generated by block copolymers. Water absorption and dielectric studies show a decrease with an increase in siloxane loading due to the combined effect both from fluorine as well as siloxane moieties in the polymer backbone. This demonstrates that the material properties can be excellently optimized by fine tuning the siloxane loading and generating the block structure in segmented block copolymers.

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