Synthesis and Characterization of Novel Hyperbranched Polyimides Based on Silsesquioxane Nanocomposite Networks

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A series of nanosized polyimides was successfully prepared by condensation polymerization of an octaamino-functionalized silsesquioxane and a series of commercially available dianhyride monomers.

The polymerization of the octaamino silsesquioxane was carried out in 1-methyl-2-pyrrolidone (NMP) at room temperature, giving poly(amic acid) as precursor polymers that were readily converted to the corresponding polyimides by thermal treatment in the subsequent step, which is similar to the conventional 2-stage method. The appropriate molar ratio of the silsesquioxane monomer to a dianhyride was 1:1. These polyimides are readily soluble in polar aprotic solvents such as 1-methyl-2-pyrrolidone, and N, N-dimethylacetamide at room temperature, and show high thermal stability with a 10% weight loss, $T_d = 441$ to 593 °C in N_2.

Key Words: Polyimides, hybrid materials, nano materials, silsesquioxanes.

Introduction

Organic polymers combined with octafunctional octahedral silsesquioxanes $[RSiO_{1.5}]_8$ (POSS) or cubic silsesquioxanes $[RSiMe_2OSiO_{1.5}]_8$ (cubes) representing 3-dimensional nanobuilding blocks have become prevalent during the past decade as a means of preparing organic-inorganic hybrid materials with precise control tailoring of nanoarchitecture and properties. A wide variety of hybrid materials with octafunctional cubes with polymerizable moieties have been prepared[1−2].

Inorganic-organic hybrid materials are expected to combine the hardness and abrasion resistance of an inorganic phase with the compliance and formability of an organic phase to produce materials that are more than simply the sum of the component parts. For this reason, it is necessary to design components that can be combined at the nanoscale[3−12].

POSS that have been functionalized with various reactive organic groups can be incorporated into virtually any existing polymer system through either grafting or copolymerization. Several POSS polymers have been prepared. Haddad[13] synthesized the styryl substituted POSS $(R_7(Si_8O_{12})(CH_2CH_2C_6H_4CH=CH_2)$

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from the incompletely condensed heptameric silsesquioxane and methacrylate-substituted POSS macromonomers have been both homo- and copolymerized. Random copolymers of norbornyl-POSS copolymers have all been synthesized via ring opening metathesis polymerization.

Laine and co-workers recently reported the nitration of the octaphenyl POSS and prepared octaaminophenyl POSS, and octaaminophenyl POSS was used with dianhyrides to prepare thermally resistant polyimide cross-linked networks[14].

Since polyimides are of great interest for high temperature applications as they exhibit extraordinary dielectric and mechanical properties at elevated temperatures[15−23], and cubic silsesquioxanes offer considerable potential for producing hybrid materials because the cube itself is the smallest particle of the inorganic phase, our goal is to develop structure-property processing relationships in nanocomposites prepared using octaamino-functionalized silsesquioxanes to establish a complete understanding of the behavior of these materials. In this approach, an organic functional group is appended to inorganic cubes via polymerization to give organic-inorganic nanocomposites wherein both components are present in the nanoscale region. Their properties will be governed not only by the nature of but also by the scale of each phase[24−25].

The effect of varying the architecture of the organic phase between cubic silsesquioxanes in these nanocomposites on their physical properties was investigated.

We chose the starting material for two reasons: (i) it is commercially available, and (ii) it has a functional end, which can be linked to a variety of dianhyride groups to prepare novel polyimides containing silsesquioxane nano building blocks. Thermally stable nanocomposites were expected and synthesized from the octaamino-functionalized silsesquioxanes and the corresponding dianhyrides using conventional 2-stage polymerization for preparing polyimides.

Experimental

FT-IR analysis was performed on a Mattson 1100 FT-IR mode spectrometer. The structural investigation of the composite material thus prepared was carried out at room temperature by Rigaku System RadB X-ray diffractometer equipped with a graphite monochromator with Cu radiation and scan rate of 1 K/min. It was used for XRD analysis of the materials.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed with Shimadzu DTA-50 and TGA-50 thermal analyzers, respectively. The DTA measurement proceeded at a heating rate of 10 °C/min. in air, whereas the TGA measurement proceeded at a heating rate of 10 °C under nitrogen.

All chemicals were purchased from Aldrich and used after purification. NMP was distilled over CaH_2 under reduced pressure and stored over 4Å molecular sieves. Reagent grade aromatic dianhydrides such as pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhyride (BPDA), 4,4′-oxydiphthalic anhydride (ODPA) that was sublimed at 250 °C under reduced pressure, and 3,3′,4,4′-biphenyltetracarboxylic dianhydride(BTDA) was used after crystallization in appropriate solvents. All the dianhydrides were dried under vacuum at 120 °C prior to use.

Inherent viscosities ($\eta_{inh} = \ln\eta_r/c$ at a polymer concentration of 0.5 g/dL) were measured with an Ubbelohde suspended-level viscometer at 30 °C using NMP as the solvent.

GPC analyses were performed at 30 °C using NMP as eluant at a flow rate of 0.5 mL/min. A differential refractometer was used as a detector. The instrument (Agilent 1100 series GPC-SEC system)

was calibrated with a mixture of polystyrene standards (Polysciences; molecular masses 200-1,200,000 Da) using GPC software for the determination of the average molecular masses and the polydispersity of the polymer samples.

Preparation of amine substituted silsesquioxane $R_8Si_8O_{12}$ (POSS-NH$_2$)

A solution of H_2N $(CH_2)_3Si(OEt)_3$ 150 mL was added to a solution of dry methanol. To this mixture was added 28 mL of concentrated HCl, and the reaction mixture was kept at 50 °C for 8 h. PtCl$_4$ (0.5% w/w of starting material) was added to this solution as a catalyst in an argon atmosphere. A crystalline precipitate formed after a day at 50 °C. It was collected and treated as described below. The product, obtained in 30% yield, was filtered, washed with cold methanol and dried in a vacuum oven at 30 °C. The product was neutralized with Amberlite IRA-400 ion exchange resin (37 g) by successive washing with NaOH (3 x 200 mL), water (6 x 200 mL) and methanol (6 x 200 mL). The amine should be prepared immediately before use or stored in MeOH solutions at -35 °C. The product melted at 220°C and the amino content was found by titration. The GPC chromatogram indicated a monodisperse compound.

Procedure for the determination of the amino content

The content of amino groups of the POSS framework was determined by consumption of HCl aqueous solutions. In a typical procedure, a 100 mL flask was charged with 0.10 g of POSS-NH$_2$ and 20 mL of 0.01 mol/L HCl aqueous solution, and the mixture was stirred at room temperature for 2 days, filtrated, and the filtrate was back titrated with NaOH (aq) using an indicator. Then the amount of terminal amino groups per 1.0 g of POSS-NH$_2$ was calculated to be 15.2%.

Synthesis of polyimides

A typical polyimide (POSS-PI-1 to POSS-PI-5) synthesis was performed as follows: octaamino-silsesquioxane (POSS-NH$_2$) (0.5 mmol) was dissolved in NMP (25 mL) in a 50 mL Schlenck tube equipped with a nitrogen line, overhead stirrer, a xylene-filled Dean-Stark trap, and a condenser. Dianhyride (4 mmol) in 5 mL of NMP was added to the amine solution and stirred overnight to give a viscous solution under nitrogen. The mixture was heated to 70 °C, xylene (5 mL) was added, and the mixture was refluxed for 3 h, followed by the removal of xylene by distillation. The mixture was transferred into an aluminum container and heated in a furnace under nitrogen atmosphere up to 130 °C at a ramp rate of 5 °C/min and kept at that temperature for 2 h. Then the sample was placed in a quartz tube and heated to several curing temperatures (100, 200, 300, 400 and 500 °C) at a ramp rate of 5 °C/min and kept at this temperature for 4 h. The yellow product was precipitated and dried at 100 °C under vacuum and then at 200-250 °C under nitrogen for 2 h; Yield, 86%.

Results and Discussion

Monomer Characterization

TGA and DTA plots for the prepared POSS frameworks are shown in Figure 1. The presence of distinctive mass-loss regions at 421 and 356 °C for POSS-NH$_2$suggest that a more complicated process took place in

all cases. The initial weight loss occurs at 300 °C and has fully subsided by 470 °C. The initial weight loss appearing at 350 °C indicating that organic segments have been decomposed, has fully subsided by 375 °C.
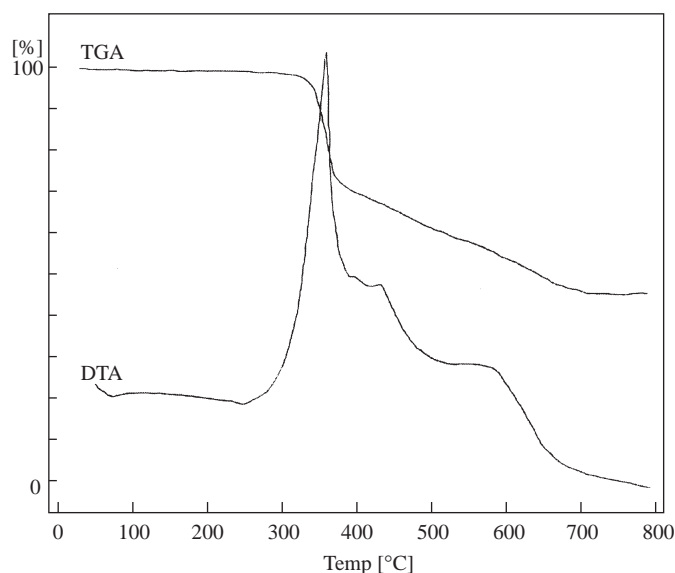
**Figure 1.** TGA and DTA thermograms of the POSS-NH$_2$.

The octaamino subsitituted framework sublimes above 400 °C. The tentative FT-IR assignments for the spectra of the frameworks were as follows: 1174 cm^{-1} (asymmetrical) v_{as} (Si-O-Si), 1060 cm^{-1}v (Si-O-), 938 and 785 cm^{-1} (symmetrical) v_s(Si-O-Si) and 620 and 550 cm^{-1}v_s (Si-O-Si). Polysiloxanes made up tetrahedral (T) units, [RSiO$_{1.5}$]$_x$, and showed a broad, structureless absorption covering the entire region of 1160–1000 cm^{-1}.

The observed XRD pattern for POSS-NH$_2$ can be fitted to a rhombohedral unit cell with the parameters $a = 1.157$ nm and $\alpha = 95.1°$. It appears that due to the hydrogen bonding formed in the case of POSS-NH$_2$, the corner substitution is not freely rotating.

Hybrid Polyimide Characterization

The inorganic segment of the hybrid materials POSS is the most thoroughly studied highly cross-linked network based on the octahedral silsesquioxane moiety as cubes[26−29]. In this work, the type of dianhyride of the organic segments is systematically varied. The resulting structures are then characterized using tools FT-IR spectroscopy, X-ray diffractometer, differential thermal analysis and thermogravimetric analysis.

The structures of the POSS and hybrid materials are depicted in Schemes 1 and 2.
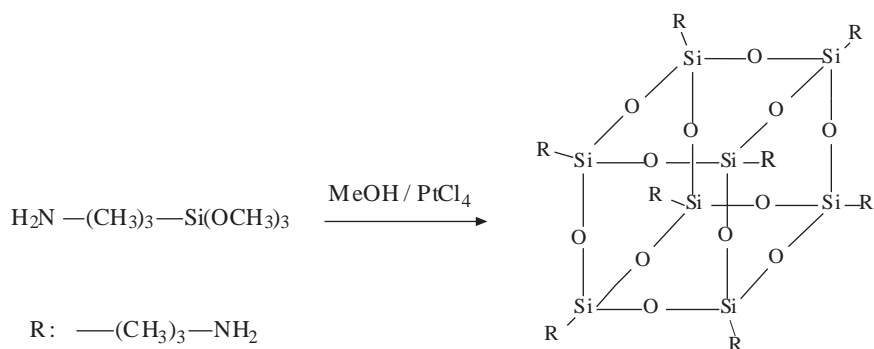
Scheme 1. The synthesis of octaaminopropylsilsesquioxanes.
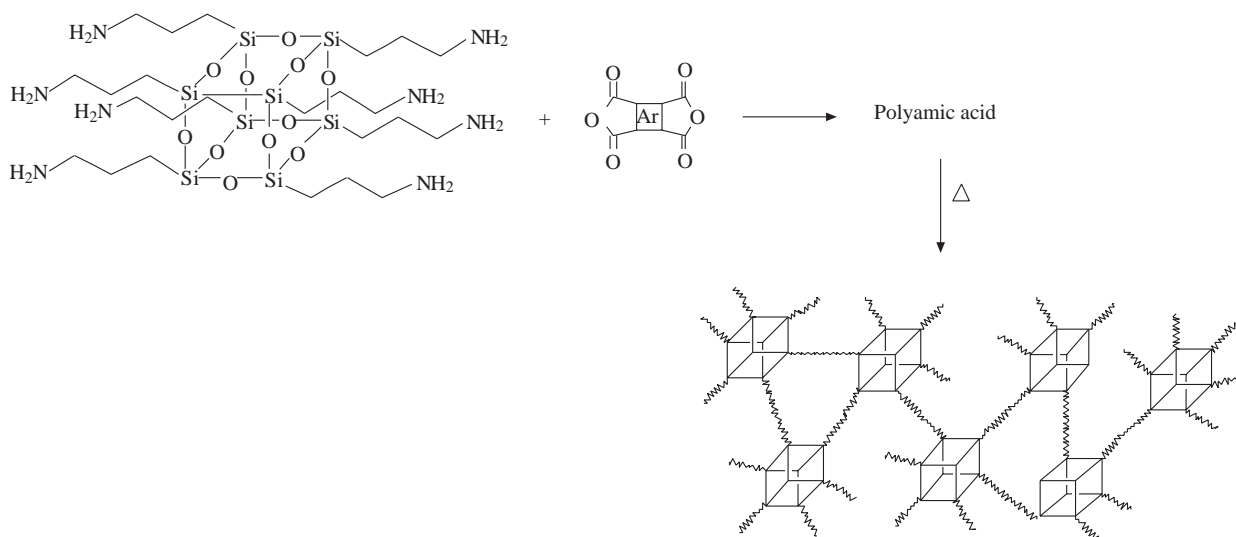
Code		Ar
POSS-PI-1	**PMDA**	Pyromellitic dianhydride
POSS-PI-2	**BPDA**	3,3′, 4,4′-benzophenonetetracarboxylic dianhydride
POSS-PI-3	**BPADA**	2,2′-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride
POSS-PI-4	**ODPA**	4,4′-oxydiphthalic anhydride
POSS-PI-5	**6FDA**	4,4′-hexafluoroisopropylidenediphthalic anhydride

Scheme 2. POSS-Polyimide hybrid material synthesis.

The infrared (FT-IR) spectra of the samples dispersed in dry KBr pellets were recorded between 4000 and 400 cm^{-1}. Imidization was confirmed by the IR spectra of the samples. The FT-IR spectra of hybrid materials containing different dianhyrides are shown in Figure 2. All the POSS hybrids present characteristics peaks at υ (C=O), 1743-1790 cm^{-1} (s) asym. imide υ(C=O) stretching, C-N imide ring stretching at 1360 cm^{-1}, aliphatic C-H stretching frequencies appeared between 2850 and 2890 cm^{-1}, 1720-1735 cm^{-1} sym. imide, whereas imide ring deformation appeared near 1050 cm^{-1} and C-N bending at 730-760 cm^{-1} [30].
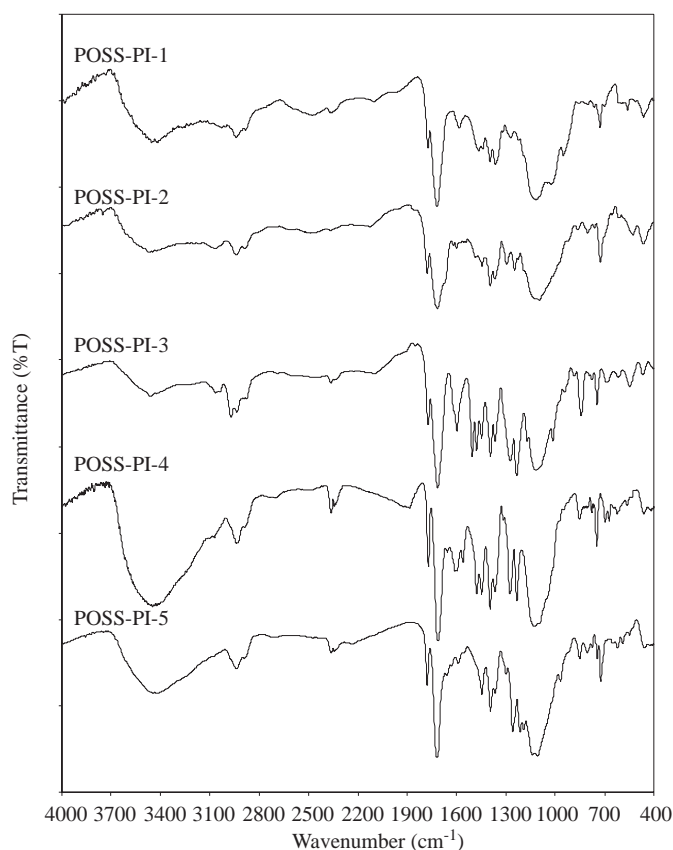
Figure 2. FTIR spectra of the hybrid materials (POSS-PI-1 to 5).

Thermal properties of the polymers were evaluated by DTA (Figure 3) and TGA (Figure 4) are listed in Table 1. The 10% weight loss in nitrogen were observed at 44 –593 °C. Typical TGA curves are shown in Figure 4. The aromatic polyimides were stable up to 500 °C. The polyimide prepared from PMDA had a relatively high thermal decomposition temperature because of its rigid structure. The 10% weight loss steps are observed below 500 °C for POSS-PI-3, POSS-PI-4 and POSS-PI-5, whereas for POSS-PI-1 and POSS-PI-2 593 and 549 °C were noted, indicating that a high degree of thermal stability was achieved if PMDA and BPDA were used as dianhyrides in the condensation process[31−35]. The ceramic char yield was over 40% in all cases, suggesting quantitative conversion of the monomers. The curing temperatures were

Table 1. Thermal properties of polyimides.

Polymer	POSS-PI-1	POSS-PI-2	POSS-PI-3	POSS-PI-4	POSS-PI-5
TGA Analysis					
On set	564	511	500	408	454
End set	628	596	556	658	590
10%	593	549	485	441	478
Char	69	74	58	43	51
IDT	538	489	408	380	393
DTA Analysis					
TDP	592	568	592	601	580
On set	551	515	540	557	535
End set	671	645	635	641	613
Heat (kJ/g)	1.64	3.32	2.28	2.69	1.93

varied between 100 and 500 °C in 100 °C increments followed by FT-IR analysis (Table 3) revealing the symmetric and asymmetric imide bands at 1790 and 1720 cm^{-1} respectively.
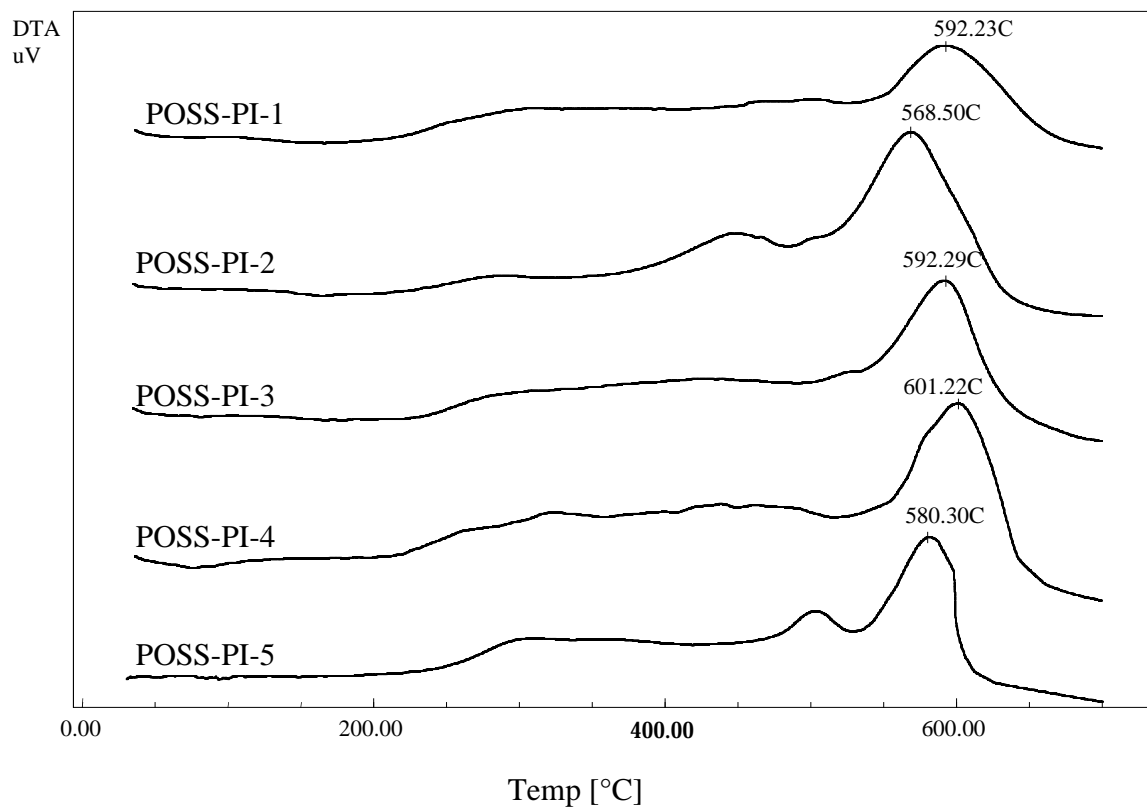
Figure 3. DTA thermograms of the hybrid materials (POSS-PI-1 to 5).
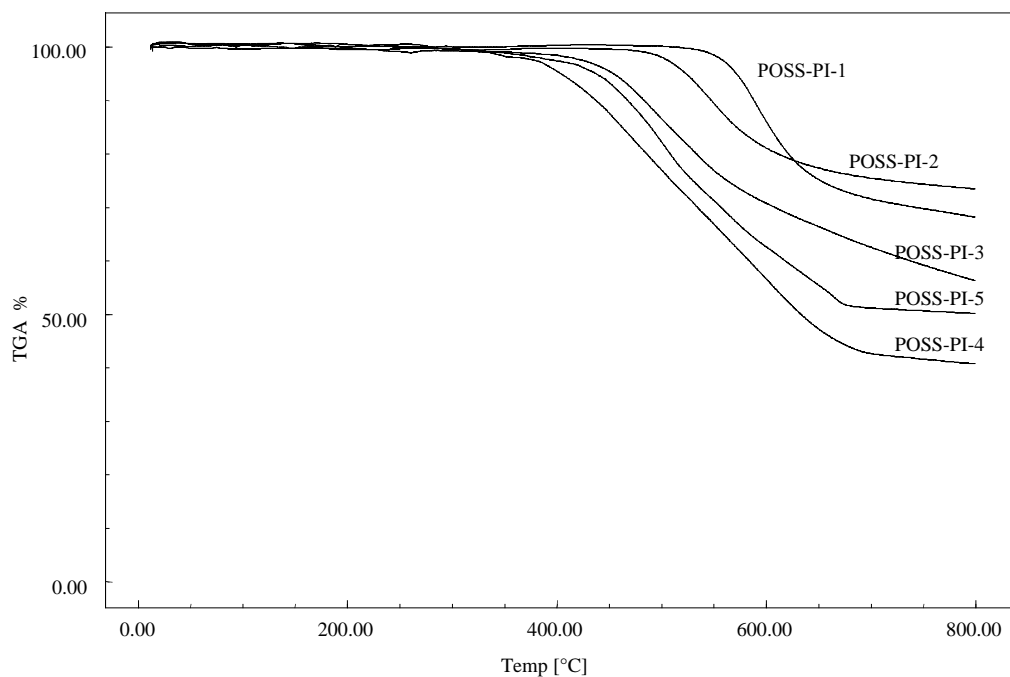
Figure 4. TGA thermograms of the hybrid materials (POSS-PI-1 to 5).

Table 2. Weight loss of curing temperature and the change in ν C-N peak of POSS-NH$_2$ and POSS-Polyimide hybrid material.

T (°C)	POSS-NH$_2$	POSS-PI-1	POSS-PI-2	POSS-PI-3	POSS-PI-4	POSS-PI-5
		The change in ν C-N peak[a] (abs)				
100	-	1.07	1.45	1.30	1.65	1.09
200	-	1.05	1.41	1.27	1.65	1.05
300	-	0.95	1.32	0.85	1.63	1.03
400	-	0.88	0.99	0.68	1.60	0.98
500	-	0.87	0.92	0.64	1.54	0.74
		% Weight loss of curing temperature in N$_2$				
100	1.826	0.236	0.527	0.286	0.594	0.318
200	2.892	0.342	0.785	0.872	0.653	0.334
300	4.011	0.461	1.260	1.212	1.246	0.767
400	29.314	0.612	1.564	2.355	5.379	2.801
500	37.541	0.728	2.765	14.346	23.83	17.776

[a] Intensity of C-N band

Table 3. Basic properties of polyimides.

| Polymer	POSS-PI-1	POSS-PI-2	POSS-PI-3	POSS-PI-4	POSS-PI-5
Yield (%)	89	82	78	91	94
d (g/cm^3)[a]	1.64	1.44	1.52	1.48	1.32
η (dL/g)[b]	2.35	2.15	2.20	2.04	1.95
Solubility [c]					
NMP	+	+	+	+	+
DMF	-	-	-	±	-
DMAc	-	-	±	±	-
Ether	-	-	-	-	-
THF	-	-	-	-	-
Hexane	-	-	-	-	-
H$_2$SO$_4$	+	+	+	+	+
DMSO	±	±	±	±	±

a. Determined by suspension method at 30 °C.

b. Measured at a concentration of 0.5 g/dL in NMP at 30 °C using an Ubbelohde viscometer.

c. (Solubility tested at 2% solid concentration; + soluble at room temperature (25 °C); ± soluble upon heating; - insoluble at room temperature).

Powder XRD studies of POSS-NH$_2$ and the POSS hybrids are given in Figure 5. POSS-NH$_2$ shows a peak at 8° 2θ that corresponds to a d spacing of 1 nm. The broadness of the peak present in all POSS hybrids can be attributed to hybrid formation in the presence of POSS inorganic segments. This broad halo present might be attributed to the Si-O-Si linkages indicating a high degree of amorphous character due to the rigid network caused by both the POSS segment and the polyimide.

Polymer POSS-PI-1 and POSS-PI-5 were largely soluble in NMP at room temperature partial solubility was observed in DMSO at room temperature in all cases (Table 3). The difference in solubility was attributed to the structure of the polymer. For instance, when PMDA was used as a condensing agent the solubility was decreased and the polyimides were not soluble in all solvents. However, when BPDA was used the solubility was increased in all cases, due to the polar carbonyl groups and the oxygen bridge.
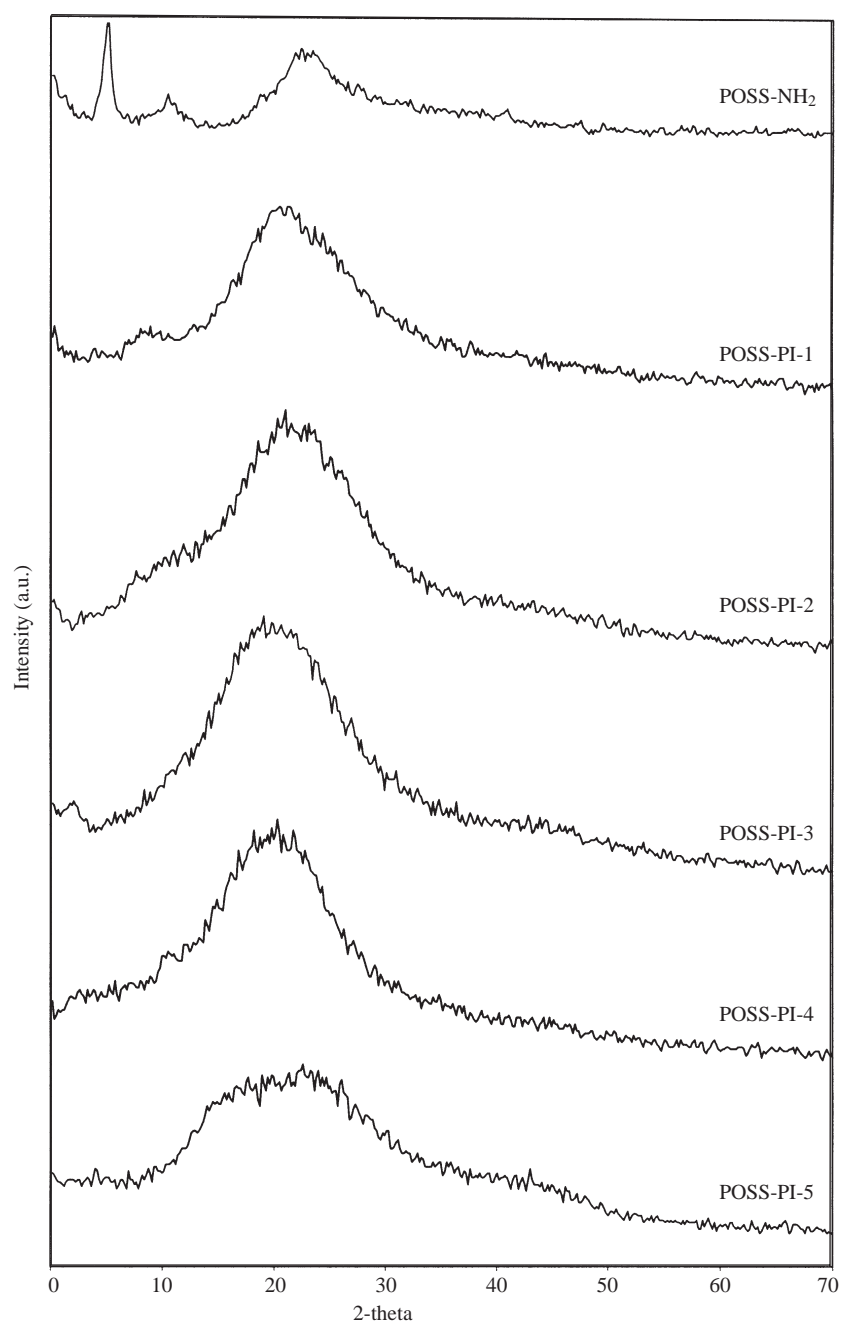
Figure 5. XRD patterns of the POSS-NH₂ and the hybrid polyimides.

Conclusion

Octaamino-silsesquioxane (POSS-NH₂) can serve as a nanobuilding block for the preparation of polyimide hybrid materials. We described herein the synthesis of novel polyimides possessing silsesquioxane moieties in which the structure of the amino precursor contains an aliphatic CH_2 unit and the corresponding dianhyrides using 2-stage polycondensation. The progress of the imide formation in all cases was studied from 100 °C to 500 °C. The polyimides were found to be stable up to 500 °C.

Acknowledgements

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