

Studies On The Synthesis And Reaction Of Silicone Anhydride Dendrimers And Thermal Properties Of Their Imides

Sangeeta Kandpal, A. K. Saxena

Abstract: Dendritic silicone core polyimides have been synthesized using silicone anhydride dendrimers which in turn were synthesized by the hydrosilation reaction of maleic anhydride with Si-H terminated silicone dendrimers in presence of Speier's catalyst. The anhydride groups were converted to imide functionality by the reaction of aromatic diamines at elevated temperatures. All the products were characterized by usual physico-chemical method i.e. elemental analysis, FT-IR and ¹H-NMR spectroscopy. The molecular weights of dendrimers were determined by using vapor pressure osmometry. The dendritic polyimides have shown fairly good solubility in polar aprotic solvents e.g. N, N-dimethylacetamide (DMAC), N, N-dimethylformamide (DMF), N methyl-2 pyrrolidone (NMP) etc. Thermal studies (TGA & DSC) of these compounds have also been studied under inert atmosphere which have shown high char yield (~ 65% at 800 °C) and thermal stability above 400 °C. The glass transition temperature of these imides was found in the range of 170-190 °C.

KEYWORDS: dendrimers; hydrosilation; Speier's catalyst; imidization; T.G.A.

1. INTRODUCTION

Polyimides are extremely useful materials which have been widely used in microelectronic industries and other advanced fields because of their outstanding properties, such as high thermal stability, mechanical properties, chemical resistance, dielectric properties and excellent tensile strength and modulus [1]. An aromatic type of polyimides (PI's) have been extensively studied in relation to the manufacture of microelectronic devices [2,3] as well as in aerospace and electronic studies [4, 5] because of their good chemical, physical and thermal properties. Polyimides are also employed as matrix resins for composite structures [6, 7]. Fiber-reinforced high temperature polyimide matrix composites offer significant advantages in structural applications over other materials because of their low density and high specific strength. These composites are attractive for use in aerospace systems, e.g., aircraft engine, airframe, missiles, and rockets, where weight is critical. This weight reduction has substantial benefits in terms of fuel savings, increased passenger or cargo load, or increased speed and maneuverability. However application of polyimides is somewhat limited due to processing difficulties, such as insolubility in conventional solvent and extremely high glass transition temperatures.

So they are carefully tailored by incorporation of flexible bonds, large pendant groups or polar substituents [8- 10] for improvement in the solubility of these materials in wide range of polar and nonpolar solvents. Now days, organic-inorganic hybrid polymers have attracted the attention of researchers greatly in view to incorporate the desirable properties of both organic and inorganic polymer in one [11]. A widely studied class of such materials is the hybrid polymers of polyimides (PIS) and silicones [12- 17] because both of these materials individually have their own peculiar properties. Silicones materials have various useful properties like low temperature flexibility, thermo-oxidative stability, hydrophobicity, biocompatibility, flame retardancy and gas permeability etc., but their mechanical and film forming tendencies are poor. polyimides with polysiloxane group as side chains were synthesized and enhancement in their thermal properties have been observed [18]. The combination of a siloxane group with an imide has not only been shown to increase the solubility of the polymer, but also used to improve its UV stability, resistance to ozone and adhesion to metals [19, 20]. Aromatic polyimide having polydimethyl siloxane side chains was also intended for the application to gas separation membranes [21, 22]. The biggest drawback associated with the imides material is the infusibility and intractability which restricts their applications. Therefore attempts were made to make meltable and soluble polyimides by various researchers. As the silicones are very good thermostable materials having excellent hydrophobicity thus have found numerous coating applications including the electronic components. So it has been considered worthwhile to make silicone core dendritic polyimides to improve their solubility and enhance processibility for a variety of coating applications. In view of it, in the present work we are reporting the synthesis of novel silicone dendrimers bearing terminal anhydride group by the hydrosilation reaction of silicone dendrimers [23] having Si-H terminals with maleic anhydride and their conversion to polyimides for making soluble and meltable hybrid organic-inorganic imides for high- tech applications.

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2. EXPERIMENTAL

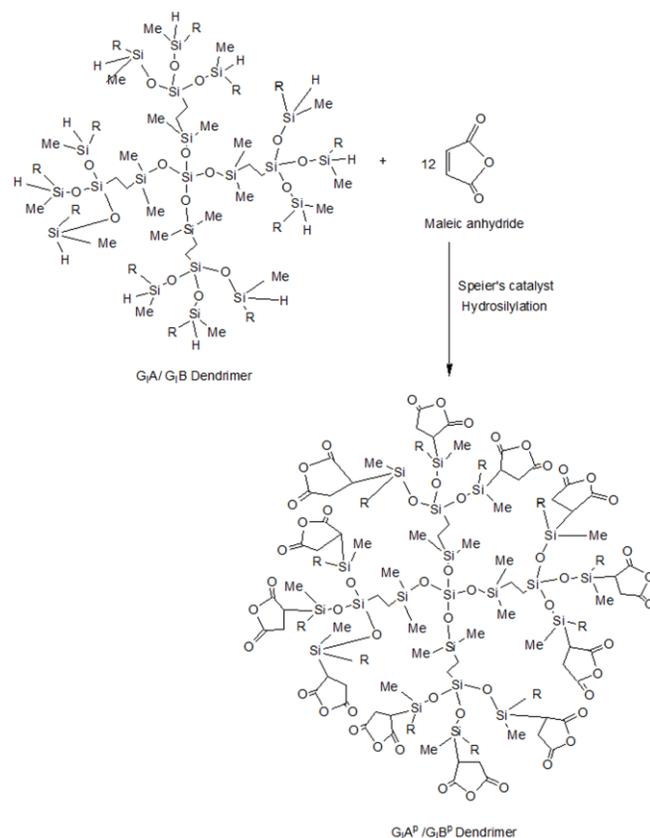
2.1 Materials

Tetrahydrofuran (THF) (LR grade, Ranbaxy), hexane (LR grade, E. Merck), petroleum ether 60–80 °C (AR grade, Samir Tech-Chem Pvt Ltd), dichloromethane (DCM) (LR grade, Ranbaxy), methyl alcohol (LR grade, Ranbaxy) were purified and dried before use as reported [24]. 4, 4'-diaminodiphenyl methane (DDM), 4, 4'-diaminodiphenylether (DDE) and 4, 4'-diaminodiphenylsulphone (DDE) were purchased from Lancaster and used as such. N, N-dimethylacetamide (DMAc), N, N-dimethylformamide (DMF), N methyl-2 pyrrolidone (NMP) and pyridine (Py) were purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieves. Maleic anhydride (LR grade, SD Fine Chemicals) was used as received. Speier's catalyst was synthesized in laboratory [25]. First generation Si-H functional G₁A and G₁B dendrimers were prepared according to reported method [23].

2.2 Synthesis of dendrimers

2.2.1 G₁A^P dendrimer

The solution of Si-H functional G₁A dendrimer (2.5 g, 1.72 mmol) and speier's catalyst (0.03 mol %) in dry THF (50 ml) was taken in a three necked round bottom flask (100 ml) fitted with a dropping funnel containing maleic anhydride (2.02 g, 20.6 mmol) was gradually added drop wise within 30 min to carry out hydrosilation reaction. The volatile substances were removed by evaporation to give pot residue. The pot residue was column chromatographed (silica gel and n-hexane) to afford yellow transparent liquid G₁A^P (C₈₈H₁₄₈O₅₂Si₂₁) dendrimer, yield 4.52 g, 89%. IR (KBr): ν 2952 (–CH₃), 2923 (–CH₂–), 2871 (–CH–), 1850 and 1781 (–CO–O–CO–, asym and sym), 1252 (–Si–CH₂–, –Si–CH₃); ¹H NMR (400 MHz, CDCl₃, δ): 0.02 (s, –Si–CH₃), 0.84 (t, –Si–CH₂–), 3.60 (d, –CH₂–CO–), 4.72 (t, –Si–CH–CO–); Anal. Calcd for C₈₈H₁₄₈O₅₂Si₂₁: C 40.18, H 5.68, Si 22.44; found: C 40.17, H 5.68, Si 22.41. Mol Wt (VPO): 2509.16 (calcd 2627.87).



Scheme 1 Synthetic route used to obtain the dendrimers (G₁A^P / G₁B^P).

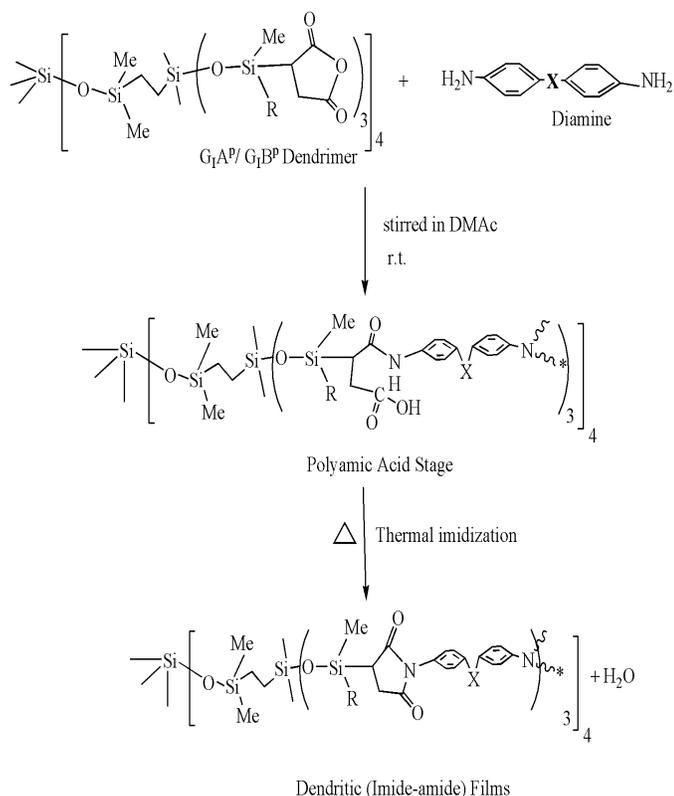
2.2.2 G₁B^P dendrimer

Hydrosilation reaction of the G₁B dendrimer (2.8 g, 1.27 mmol) with maleic anhydride (1.49 g, 15.2 mmol) in presence of speier's catalyst were carried out same as the hydrosilation of G₁A^P dendrimer, to afford the yellow transparent liquid G₁B^P (C₁₄₈H₁₇₂O₅₂Si₂₁) dendrimer, yield 4.28 g, 91%. IR (KBr): ν 2960 (–CH–), 2922 (–CH₂–), 1841 and 1781 (–CO–O–CO–, asy and sym), 1495 (–Si–Ph), 1261 (–Si–CH₃), 1054 (–Si–O–Si–); ¹H NMR (400 MHz, CDCl₃): –0.01(s, –Si–CH₃), 0.82 (t, –Si–CH₂–), 7.3–7.5 (m, aromatic protons), 2.82 (d, –CH₂–CO–), 5.2 (t, –Si–CH–CO–); Anal. Calcd for C₁₄₈H₁₇₂O₅₂Si₂₁: C 52.70, H 5.13, Si 17.49 found: C 52.69, H 5.14, Si 17.50. Mol Wt (VPO): 3257.43 (calcd 3372.74).

2.3 Preparation of dendritic imide's (DI) films.

2.3.1 Synthesis of PAAs (polyamic acids)

General procedure to prepare the dendrimers poly amic acid solution is as follows: A three necked flask was charged with anhydride dendrimer (1.5 gm, 0.57 mmol) and DMAc (25ml). The solution was stirred at room temperature under a nitrogen atmosphere until the anhydride mixes homogeneously into the solvent. A solution of diamine (0.678 gm, 3.42 mmol) (DDM/ DDE/ DDS) in DMAc (10.0 ml) was added dropwise to the reaction mixture. The mixture was stirred at room temperature for 24 h under a nitrogen atmosphere to form a viscous poly (amic-acid) solution. The other dendrimer's PAA solutions were prepared by the same procedure using the appropriate diamines.



Scheme 2 -Synthetic route used to obtain the dendritic polyimides. (Where X= CH₂, O, SO₂).

2.3.2 Thermal treatment of PAAs (polyamic acids)

The solution of polyamic acid in DMAc was cast in Teflon petri dishes. Solvent elution was carried out at 70°C for 12 h and then at 80°C for an additional 2h under vacuum. Imidization was carried out by successive heating at 100°C, 200°C and 300°C each for 1 h under nitrogen.

2.4 Instrumentation

Fourier transform infrared spectroscopy (FT-IR) was used to characterize the functional group and monitoring the reaction progress of different dendrimers. Infrared spectra of the sample were recorded on a Perkin Elmer FT-IR spectrometer RX1 at room temperature using KBr pellets. The analysis was performed between 500 and 4000 cm⁻¹. ¹H nuclear magnetic resonance spectroscopy spectra were recorded at room temperature on a Bruker Avance 400 MHz NMR spectrometer. Samples (5-10 mg) for NMR analysis were dissolved in deuterated chloroform (CDCl₃). Vario EL III CHNOS elemental analyzer was used for elemental analysis of dendrimers and silicone elemental analysis was carried out according to reported method [24]. Vapour pressure osmometre (VPO) was performed to determine molecular weight of dendrimers using a Knauer-7000 in toluene at 60°C in a concentration range of 5-10 mg/ml. and polystyrene in the range of 2500-3500 was used for calibration. Differential Scanning Calorimetry (DSC) analysis was performed on a TA Instruments Q 100 DSC. All measurements were conducted in crimped aluminium pans under a nitrogen atmosphere, at a purge gas flow rate of 50 ml/min. samples were heated from 25 to 300°C at a rate of 10°C/min. samples were then cooled

from 450- 25°C. Finally, the samples were heated for a second time at rate of 10°C/min to 450°C. Thermogravimetric analysis (TGA) was performed on a TA Instruments Hi-Res TGA 2950 thermogravimetric analyser in a nitrogen atmosphere. Approximately 5-10 mg of each sample was heated from 25-800 °C at a rate of 10°C/min.

3. RESULTS AND DISCUSSION

High char yield; flame retardants and thermo oxidative stable materials are very much required to prepare high performance FRP composites insulating material for electronics and other high tech applications. Hence in continuation of our previous work, we have synthesized silicone anhydride terminal dendrimers in high yield which on addition to aromatic diamines yielded dendritic silicone imides. These imides are soluble in common polar aprotic solvents. So they can be used as resin matrix, coating substrates in electronic and aerospace applications. In present work the hydrosilation of the Si-H functional G₁A & G₁B dendrimer were carried out with maleic anhydride in presence of speier's catalyst to synthesize anhydride functional dendrimers (G₁A^P/G₁B^P) (Scheme 1). Further imide derivatives of the silicone dendrimers have been synthesized using precursor synthetic route i.e. poly (amic acid) (PAA) followed by thermal imidization [26- 29] reaction (scheme-2). The structures of dendrimers were confirmed by FT-IR, ¹H NMR, elemental analysis and vapour pressure osmometry. Thermal behaviour of imide's films was characterized by thermogravimetric analysis.

3.1 FTIR spectroscopy

FT-IR spectra of the compound have been showed in the figure-1. In all dendrimers an IR absorption peak appeared at ~1078cm⁻¹ which indicate the presence of ν_{Si-O-Si} bond. The hydrosilation reaction of G₁A and G₁B dendrimer with maleic anhydride were carried out to prepare G₁A^P and G₁B^P dendrimers, the ν_{Si-H} peak at 2135 cm⁻¹ of Si-H functional dendrimer and ν_{C=C} peak at 1594 cm⁻¹ of maleic anhydride disappeared which confirmed the addition of Si-H group on maleic anhydride. The presence of ν_s and ν_{as} at ~1781 and ~1849 cm⁻¹ showed that the anhydride group was intact in the dendrimer. Further in the imidization reaction of the G₁A^P and G₁B^P dendrimers with different aromatic diamines were carried out via polyamic acid as intermediate it is further treated thermally to produce DI's films. The formation of PAA was observed with the appearance of peak at ~1681 cm⁻¹ is due to ν_{C=O} stretching and disappearance of sym. and asym. stretching peak of anhydride at ~ 1781 and ~ 1852 cm⁻¹ respectively. The IR absorption peak at 1777 cm⁻¹ and 1718 cm⁻¹ as appeared in the product, these peaks corresponded to asymmetrical and symmetrical stretching of carbonyl group of imide ring. The spectra also showed absorption peak at ~ 1368 cm⁻¹ which may be assigned due to ν_{C-N-C} bond stretching of imide ring.

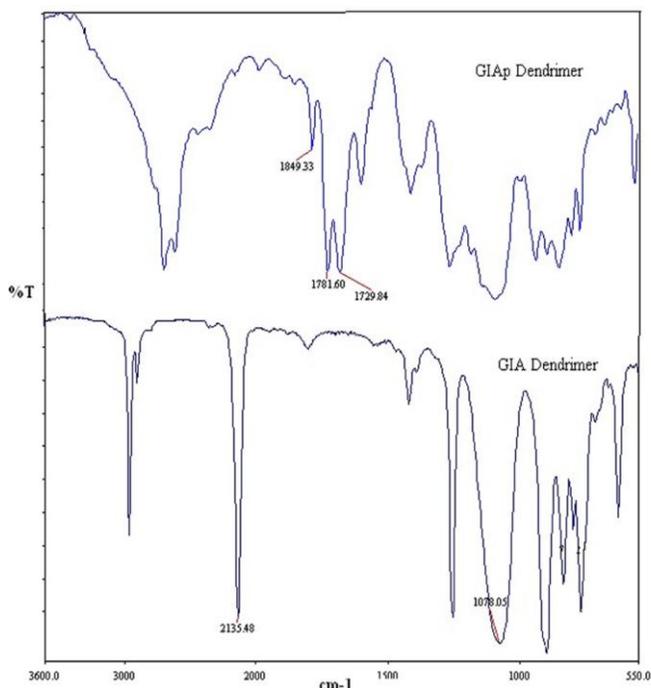


Fig. 1 FT-IR spectra of Dendrimers (G_1A , Si-H functional and G_1A^P , Si-anhydride functional).

3.2 NMR spectroscopy

1H NMR spectra of dendrimers G_1A and G_1B respectively showed multiplet for δ Si-H at ~ 4.74 ppm due to coupling with Si-Me and Si-Ph protons. The progress of hydrosilation of dendrimer G_1A and G_1B with maleic anhydride was confirmed by disappearance of Si-H proton at ~ 4.74 ppm and HC=CH proton at 5-6 ppm. The presence of anhydride groups in G_1A^P / G_1B^P dendrimers were confirmed by (d, $-CH_2-CO-$) proton at ~ 2.82 - 3.8 ppm and δ (t, $-Si-CH-CO-$) proton at ~ 4.7 - 5.2 ppm.

3.3 Thermal Analysis

The thermal properties of these dendrimers were evaluated by means of TGA & DSC. Figure 2 shows the TGA curves for different dendritic imide films and Table 1 gives the temperatures for the required weight loss values. The graph shows single stage degradation behaviour. The onset temperature of the imide's films has been found in the range 280-320°C. Taking 10 wt. % losses as thermal decomposition temperature, it is found that DI's films decompose at around 425 °C. And maximum weight loss was found at ~ 550 °C. The char yield of the DI's films is very high. It is found in the range of 55-65% at 800 °C in inert atmosphere thus may be deemed as good flame retarding materials. The dendritic imides films showed the glass transition temperature (T_g) in the range of 170-190 °C, depending on the structure of amine and dendrimer used.

Table 1 TGA data of resulting dendritic imides (DI's) films.

SN	Dendritic Imides	$T^{a}_{10\%}$ (°C)	$T^{b}_{max\%}$ (°C)	Char Yield (%)	T_g^c (°C)
1	DI _a	423	541	48	180
2	DI _b	487	548	55	190
3	DI _c	504	565	58	189
4	DI _d	465	585	63	174
5	DI _e	432	531	65	177
6	DI _f	415	525	69	178

a $T_{10\%}$ (10% decomposition temperature).

b $T_{max\%}$ (maximum decomposition temperature).

c T_g (glass transition temperature).

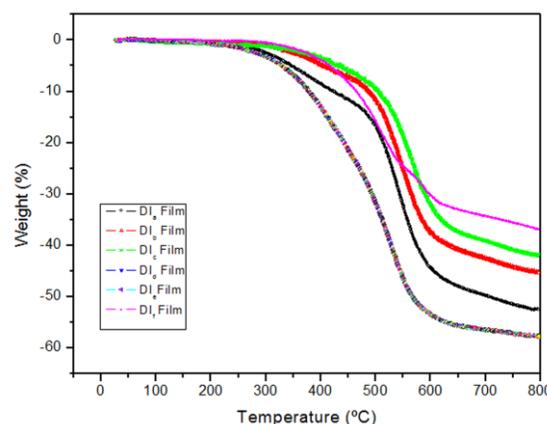


Fig. 2 Thermogravimetric analysis of dendritic imides.

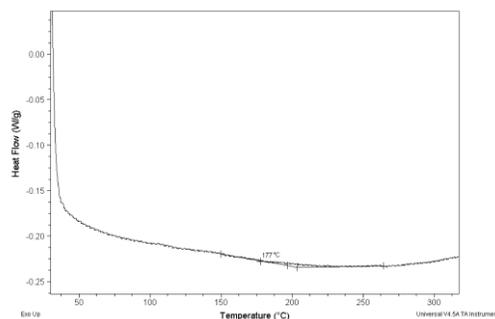


Fig. 3 DSC curve of dendritic imide (DI_e).

3.4 Films Solubility

One of the major objectives of this work is to study the solubility and the flexibility of these dendrimers by incorporating the soft segments in their core. Their solubility was tested quantitatively in various solvents and the results are summarized in table-2. Having soft segment Si-O-Si in the dendrimer its solubility will increase so these imide showed very good solubility in solvent such as DMF, DMAc, NMP and H_2SO_4 at room temperature. They are insoluble in solvent such as chloroform, dichloromethane and methyl alcohol etc.

Table 2 Solubility of dendritic imides.

S.N.	Dendritic Imides	THF	Methanol	DCM	DMF	DMAc	NMP	Pyridine
1	DI _a	–	–	–	+-	++	++	+-
2	DI _b	–	–	–	+-	+-	++	+-
3	DI _c	–	–	–	+-	+-	++	+-
4	DI _d	–	–	–	++	+-	++	+-
5	DI _e	–	–	–	++	++	++	+-
6	DI _f	–	–	–	++	++	++	+-

a) Symbols: ++ soluble, +- soluble by heating or partially soluble, – insoluble.

b) DMF: dimethylformamide, NMP: N-methyl-2-pyrrolidone; THF: tetrahydrofuran, DCM: dichloromethylene, DMAc: N, N-dimethylacetamide

4. CONCLUSIONS

In this study the novel silicone core anhydride functional dendrimers were successfully synthesized in high yield via hydrosilation reaction. Thermal imidization of the anhydride containing dendrimers with different aromatic diamines was done to synthesize dendritic imide films. Thermal studies of the dendritic imide films were shown high thermal stability ($T_d > 500$ °C in nitrogen) and very good char yield upto 65%. These imide films have shown good solubility in polar aprotic solvents. It proves that these novel dendrimers can further used for resin matrix and coating substrates for different electronic and aerospace high-tech applications.

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