Thermal aspects of Kumada rearrangement in symmetrical and asymmetrical polysilanes-Interdependence of molecular structure, thermal degradation, and stability

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Abstract

Thermal degradation behavior, exothermic patterns, and kinetic parameters of symmetrical/asymmetrically substituted polysilanes during the Kumada thermal rearrangement in the temperature range of 100-450 °C, were investigated applying thermogravimetric (TGA) and differential scanning calorimetric (DSC) techniques. Three kinds of polysilanes, viz., Polydimethylsilane (PDMS), Polydiphenylsilane (PDPS) and Polymethylphenylsilane (PMPS) were synthesized through Wurtz/Wurtz-Fittig polycondensation. As-synthesized polysilanes were then characterized by FT-IR, CHNO, and TGA-DSC techniques. FT-IR spectra confirmed the presence of methyl, phenyl, and a combination of methyl-phenyl functional groups in PDMS, PDPS, and PMPS, respectively. From CHNO analysis, the chemical/empirical formula of PDMS, PDPS, and PMPS was found to be $SiC_{2.01}H_{6.25}$, $SiC_{12.50}H_{10.26}$, and $SiC_{6.45}H_{7.76}$, respectively. TGA results confirmed that PDPS was more thermally stable as compared to PDMS and PMPS. The kinetic parameters of polysilanes were determined by using isoconversional methods such as Ozawa and modified Kissinger-Akahira-Sunose (KAS) methods. The average value of activation energy for PDPS obtained from Ozawa and KAS methods was found to be 1078.49 and 1068.32 kJ/mole, respectively, which is very much higher as compared to that of PDMS and PMPS.

1. Introduction

Polysilanes are a special type of inorganic polymers having a catenated silicon linear backbone structure with hydrogen, alkyl, vinyl, and aryl organic functionalities as side groups. The elemental composition of the main chain and the nature of side groups determines the physical and structural properties in the polymeric state and the resulting ceramic. Similar to carbon-based polymer chains, which consist of entirely carbon atoms, the silicon element is almost unique and can homocatenate to form stable linear chains. The properties of these consecutive -Si-Si- chains vary significantly as compared to that of carbon catenates [1, 2]. Polysilanes polymers having different substituent groups exhibit unique optical and electronic properties that are not observed in the case of polymers with carbon skeletons [3]. The highly unusual features of polysilanes are due to the continuous chains of silicon atoms present in their structure, which allows significant delocalization of electrons along the polymer chain [4, 5]. The molecular structure of the polymer system defines the rigidity of the polymer chain. It affects the optical properties of the polymeric material, which are very much crucial in the case of the photolithographic process [6]. Recently polysilanes have emerged as a new class of pre-ceramic polymers that can be converted into a ceramic component with very high green density. Till now, the synthesis of various types of polysilanes polymers containing different substituent groups have been reported, and their structural properties were studied extensively by using X-ray diffraction, Raman spectra, temperature-dependent U.V. spectra, and I.R. spectra, etc. Because of the unusual features of polysilanes such as electrical, photo-electronic, non-linear optical properties, semiconducting, and thermal properties [7], they are widely used for a variety of applications. For the first time, kipping reported the synthesis of diaryl polymer, i.e., poly(diphenyl silane) through Wurtz reductive dehalogenation reaction by using dichlorodiphenylsilane as starting material [8]. Later in 1950, Burkhard reported the synthesis of di-alkyl derivatives by following the same route as Kipping [9]; however, the resultant polymers were characterized as white powders and found to be insoluble in many organic solvents, it was also observed that the consequent white powder started to decompose without melting when it is heated above 250°C (also known as intractable material) and evoked less scientific interest. Polysilanes are used as thermal precursors for synthesizing ceramic materials [10, 11], which was initially proposed by Yajima and his co-workers by successfully transforming polydimethylsilane to β-SiC fibers with a proper heat treatment process [12].

Polysilanes are synthesized through various synthetic procedures such as anionic polymerization of masked disilanes [13], a dehydrogenative coupling of primary silanes [14], and ring-opening polymerization of strained cyclosilanes [15]. However, despite the above procedures, Wurtz reductive dehalogenation of dichloroorganosilanes remains as most followed and standard method for the synthesis of polysilanes [16]. But, after three decades, tractable and soluble polysilanes of higher molecular weight were synthesized [17–19], and they have attracted the attention of many scientific researchers in the nature of bonding in silicon chains. The fundamental investigation of symmetrical/asymmetrical polysilanes is an essential and necessary research topic to gain a better understanding of thermal rearrangement behavior during Kumada condensation, which transforms oligomeric silane to polymeric carbosilanes. Therefore, the characterization of the pyrolysis process and thermal decomposition mechanism of the polymer is very much essential for the control and optimization of the production processes for liquid, solid, and ultra-high molecular weight polycarbosilanes (PCS).

The knowledge about the thermal decomposition of polysilanes assume significance from an industrial point of view as the temperature, and U.V. light radiation are critical parameters in the fields, as mentioned above. This will not only help us to know the behavior of polysilanes at high temperatures but also helps in selecting the right type of polymer for a specific application where high temperatures are encountered. Watanabe et al. found that the heat treatment of Poly (phenyl silane) under U.V. irradiation leads to its conversion to Silica [20]. Among all the available thermal analysis techniques, the thermal decomposition, kinetics, and degradation mechanisms of the polymers can be well explained by using TGA and DSC techniques. Recently many papers have reported different types of kinetic methods such as single heating and multi-heating methods for the analysis and interpretation of thermal data obtained from TGA or DSC techniques [21–23]. Although some literature has been reported on the photo-degradation of linear and cyclic polysilanes, to the authors' best of the knowledge till now almost no/very few reports have been reported regarding the structural information, thermal behavior and thermal degradation kinetics and mechanisms of polysilanes. AK Saxena et al., investigated the thermal degradation behavior of some copolysilanes to assess their thermal stability [24]. Therefore, the present work deals with the syntheses of a series of symmetrical and asymmetrical polysilanes, namely PDMS, PDPS, and PMPS, and their structural characterization; thermal behavior at high temperatures was studied applying non-isothermal thermogravimetric analysis. Their relevant kinetic parameters were calculated by using isoconversional methods such as Ozawa and modified KAS method to understand the influence of different functional substituents during Kumada thermal rearrangement. Various kinetic methods for the calculation of kinetic parameters, as suggested by the kinetics committee of the international confederation for thermal analysis and calorimetry (ICTAC), were followed in this investigation [25].

2. Experimental

2.1. Materials and Methods

Three monomers were used in the present study for the synthesis of polysilanes, i.e., Dichlorodiphenylsilane (97%, Sigma Aldrich), Dichlorodimethylsilane (Spectro-Chem) and Dichloromethylphenylsilane (98%, Alfa Aesar). They were received in a tightly sealed amber-colored bottle, and they were used without any further distillation. Metallic Sodium (SDFCL, Mumbai) dispersion in Anhydrous Toluene (99.8%, Merck) was done by using a specially designed reactor. Methanol (A.R., Nice chemicals), n-Hexane (AR, 99%, SDFCL), and DI water were used as solvents during the synthesis of PDMS, PDPS, and PMPS. All the solvents in the present study were used as received without any further purification.

2.2. Synthesis of symmetrical/asymmetrical polysilanes

Dichlorodimethylsilane (DCDMS) monomer was used as a precursor for the synthesis of PDMS. It was reacted with metallic sodium dispersion in THF at a temperature range of 100–120°C under an inert atmosphere, as shown in scheme 1. Initially, a 2mm x 2mm chopped metallic sodium small pieces were introduced into THF in a 4-necked reaction flask under nitrogen atmosphere. The resultant solution was maintained at a temperature of 100°C. Proper dispersion of metallic sodium particles in THF was ensured by simultaneous heating and stirring operations.

Sodium pieces thus melted at a temperature of 98°C and settled at the bottom of the reactor. After the proper dispersion of sodium in THF, the Dichlorodimethylsilane monomer was then added dropwise into the reaction flask, and stirring was done continuously to ensure the adequate dechlorination reaction to take place. The reaction mixture was continuously refluxed at 120°C for 8 h, and then it is allowed to cool to room temperature overnight. Deactivation was done to deactivate the un-reacted residual sodium in the reaction flask by using tertiary alcohol, followed by vacuum filtration with DI water. The final white precipitate was then dried at 120°C for 2 hours in a hot air oven. For the synthesis of PDPS and PMPS, the same experimental procedure was followed by using Dichlorodiphenylsilane (DCDPS) and Dichloromethylphenylsilane (DCMPS) as starting materials, respectively. The chemical structures of the synthesized polysilanes are shown in scheme 2. The synthesis reaction recipe of substituted polysilanes and yield were presented in Table 1.

Table 1
Synthesis recipe and yield of symmetrical/ asymmetrical polysilanes

Polysilanes	Sodium (PPW)	Monomer (PPW)	Yield (%)
PDMS	110	205	81
PDPS	36	200	74
PMPS	48	200	68

2.3. Fourier transform- infrared analysis (FT-IR)

FT-IR analysis of symmetrical/asymmetrical polysilanes was carried out by using Nicolet 6700 FT-IR spectrophotometer (Make: Thermo Fisher Scientific, USA) for the confirmation of functional groups present in as-synthesized polysilanes. The typical conditions were as follows: Frequency range: 4000 – 400 cm^{-1}, resolution: 2 cm^{-1}, scanning: 32 counts and purging gas N_2 (flow rate 50 ml/min). KBr pellet method was used for the analysis, in which the pellets were prepared by compressing a finely ground mixture of about 100 mg of KBr powder with 2 mg of sample.

2.4. Elemental analysis

The amount of carbon, hydrogen, and silicon elements present in symmetrical/asymmetrical polysilanes were estimated using Perkin-Elmer 2400 series CHN analyzer. The thermal combustion method was used for the determination of carbon and hydrogen contents present in the polymer samples. About 2 mg of the sample was taken in a tin container, and was heated in the combustion tube at 1800°C under oxygen atmosphere. The amount of carbon and hydrogen present in the sample was measured in the form of CO_2 and H_2O by gas chromatography. For the determination of Si content in the sample, approximately 10 mg of polymer sample was fused with a mixture of KNO_3 and KOH in a nickel crucible at 650°C to release silicate and then it was detected by using atomic absorption spectroscopy.

2.5. Thermo-gravimetric analysis (TGA)

Thermal behavior or thermal decomposition of symmetrical/asymmetrical polysilanes from room temperature to 400°C was evaluated by using Q500 thermogravimetric analyzer (T.A. instruments-UK model). Approximately 8 mg of polymer samples were placed in a platinum macro pan with an empty pan as a reference, and were analyzed at various heating rates of 4, 8, and 12°C/min. Nitrogen flow was used before and during pyrolysis, with a flow rate of 50 ml/min.

2.6. Differential scanning calorimetry analysis (DSC)

The nature of the evolution of exothermic heat, which occurs as a part of thermal-oxidative reactions of symmetrical/asymmetrical polysilanes, was estimated by using DSC 821e differential scanning calorimeter (Make: Mettler Toledo). About 8 mg of sample was placed in an aluminum pan, and it was scanned from room temperature to 400°C at a heating rate of 8°C/min under high purity argon with a flow rate of 50 ml/min.

3. Results And Discussion

3.1. Structural elucidation through FT-IR analysis

The identification of functional groups present in polysilanes carried-out by applying the FT-IR method, and the resulting peak assignments are presented in Table 2. Figures 1(a)-1(c) shows the FT-IR spectra of the polysilanes according to the kinds of side chains present in their molecular structure. The FT-IR spectrum of PDMS showed the characteristic peaks corresponding to methyl group at 2956, 2894, and 1406 cm^{-1} that is attributed to C-H asymmetric, C-H symmetric, and C-H bending vibrations in methyl group, respectively. The absorption peaks at 1248 and 629–829 cm^{-1} corresponds to Si-CH_3 stretching and bending vibration, respectively, which indicates that the synthesis of PDMS was successful On the other hand, the FT-IR spectrum of PDPS exhibited a different set of peaks corresponding to the phenyl group as compared to that of PDMS. The peaks at 3067, 3046,1482 and 1426 cm^{-1} are due to C-H asymmetric, C-H symmetric, and C-C stretching vibrations in phenyl group, the small peaks at 1955, 1881 and 1821 cm^{-1} are overtone peaks of the phenyl group. Finally, the peaks at 1098 and 734 & 696 cm^{-1} are assigned to Si-C_6H_5 stretching, and bending vibrations indicate the presence of phenyl group side chains in PDPS. From the FT-IR spectrum of PMPS, it was observed that PMPS contained characteristic peaks corresponding to both phenyl and methyl groups, as mentioned in PDPS and PDMS, which confirms that the formation of PMPS.

Figure 2 shows the comparisons of intensities of different characteristic peaks present in PDPS, PMPS, and PDMS. The phenyl characteristic peaks, i.e., at 1482, 1426 and 1098 cm^{-1} are present in both PDPS and PMPS, but their intensities are lower in the case of PMPS as compared to PDPS because PMPS has only single phenyl ring linked to a silicon atom, whereas, PDPS consists of two phenyl rings on either side of the silicon atom. Similarly, the difference between PMPS and PDMS can be explained by using methyl characteristic peak, i.e., at 1248 cm^{-1},whose intensity is higher in the case of PDMS because of the presence of methyl groups on either side of Si atom.

Table 2

FT-IR peak assignments of symmetrical/asymmetrical polysilanes

Polysilanes Kind	Wave number (cm^{-1})	Modes of vibrations
PDMS	3424	OH stretching vibrations
PDPS	2956	CH asymmetric vibrations in Si-CH_3
PMPS	2894	CH symmetric vibrations in Si-CH_3
	1597	OH bending vibrations
	1406	CH bending in Si-CH_3
	1248	Si-CH_3 stretching vibrations
	1033	Si-O-Si stretching
	629–829	Si-CH_3 bending vibrations
	3450	O.H. stretching vibrations
	3067	C.H. asymmetric vibrations in Si-C_6H_5
	3046	CH symmetric vibrations in Si-C_6H_5
	1954,1881 and 1821	Overtones in the phenyl group

Polysilanes Kind	Wave number (cm^{-1})	Modes of vibrations
	1482 and 1426	C-C stretching vibrations in phenyl group
	1096	Si-C_6H_5 stretching vibrations
	734 and 696	Si-C_6H_5 bending vibrations
	3450	OH, stretching vibrations
	3067	C.H. asymmetric vibrations in Si-C_6H_5
	3046	CH symmetric vibrations in Si-C_6H_5
	2956	CH asymmetric vibrations in Si-CH_3
	2894	CH symmetric vibrations in Si-CH_3
	1955,1881 and 1821	Overtones in the phenyl group
	1482 and 1426	C-C stretching vibrations in the phenyl group
	1248	Si-CH_3 stretching vibrations
	1098	Si-C_6H_5 stretching vibrations
	629–781	Si-CH_3 bending vibrations
	734 and 696	Si-C_6H_5 bending vibrations

3.2. Elemental analysis

CHN analysis was done for the determination of the chemical composition of symmetrical/asymmetrical polysilanes, and wt (%) of each element present in the synthesized polysilanes are presented in Table 3. The empirical formula of as-synthesized PDMS, PDPS, and PMPS was found to be $Si_{1.0}C_{2.01}H_{6.25}$, $Si_{1.0}C_{12.50}H_{10.26,}$ and $Si_{1.0}C_{6.45}H_{7.76,}$ respectively.

Table 3 Silicon, Hydrogen, and carbon contents of polysilanes

Polysilanes Kind	Elemental composition (wt %)					
	Si		C		H	
	Found	Calculated	Found	Calculated	Found	Calculated
PDMS	47.9	49.2	41.3	40.7	10.8	10.1
PDPS	14.9	15.9	79.6	78.7	5.5	5.4
PMPS	24.9	23.9	68.2	69.4	6.9	6.7

3.4. Thermo-gravimetric analysis (TGA)

TGA investigated the thermal stability, degradation, and mass loss behaviors of symmetrical/asymmetrical polysilanes at a heating rate of 4, 8, and 12°C/min in the temperature range of 25–400°C under N_2 atmosphere. TGA graphs of polysilanes at different heating rates are shown in Fig. 3 (a) – 3 (c).

From Fig. 3(a) we can observe that PDMS decomposition started at 220°C, and more than 50% mass loss was observed at 400°C. The mass loss in this region can be attributed to radical cleavage of repeating Si-Si linkages of polymer backbone followed by de-polymerization, which leads to the formation of oligomeric products. Whereas in PMPS, the starting point of decomposition temperature has shifted to a higher temperature of 286°C. A higher mass loss was observed in the case of PMPS compared to that of PDMS due to the radical cleavage of Si-Si bonds because of their lower bond energy as compared to that of a C-C bond. Finally, a further shift in the starting point of decomposition temperature to 306.04°C was observed in PDPS, and more than 70% residual mass was left at 400°C. PDPS exhibited higher residual mass loss when compared to PDMS and PMPS because of the presence of two phenyl groups on either side of the silicon atom. As phenyl ring requires higher energy for decomposition or melting to take place because of its higher molecular weight compared to that of a methyl group, this makes PDPS more thermally stable compared to that of PDMS and PDPS. Mass loss and residual mass of synthesized polysilanes at different heating rates are shown in Table 4.

Table 4
TGA data of polysilanes

Heating Rate °C/min	Polysilane Kind	Temperature Range °C	Mass loss Wt. %	Residual mass Wt. %
4.0	PDMS	226 – 402	51.00	49.00
	PDPS	209 – 402	26.77	73.23
	PMPS	253 – 402	62.50	37.50
8.0	PDMS	226 – 402	49.00	51.00
	PDPS	209 – 402	17.40	82.60
	PMPS	253 – 402	42.00	57.90
12.0	PDMS	226 – 402	47.20	52.80
	PDPS	209 – 402	14.00	86.00
	PMPS	253 – 402	31.10	68.90

3.5. Differential scanning calorimetric analysis (DSC)

DSC exothermal patterns, as evident from the thermal analysis of PMPS, PDPS, and PDMS samples, are shown in Figs. 4(a-c), where the characteristic thermal peaks and troughs are illustrated. The pendant functional groups substituted on the linear primary chain influence the thermal properties of polymers significantly. As shown in Fig. 4(a), the DSC curve of PMPS exhibits two successive weak exothermic peaks at temperature T_1(265°C) and T_2(350°C), corresponding to first and second order glass transition points.

This is followed by a deep melting curve beginning at T_3 (400°C) with complete melting at T^4 (410°C). Similarly, DSC Exotherm of PDPS two softening temperatures at T1(190°C) and T2(260°C), followed by two exothermic peaks at T_3 (290°C) and T_4 (350°C). The melting curve begins at 370°C. A weak and broad exothermic peak at 350°C in both PDPS and PMPS represents the energy released by the polymer chains to move into ordered arrangements or for the rearrangement of molecular chains followed by melting which is exhibited as the sharp endothermic peak at 377.5°C in PDPS and a weak endothermic peak at 385°C in PMPS. PDMS shows a weak decomposition at T_1 around 190°C, followed by a distinct and robust melting curve starting at T_2 (340°C) and complete melting at T_3 (370°C), which is characteristic of PDMS. From the above exothermic patterns, It is evident that PDMS and PDPS may be more flexible and elastic polymer as compared to PMPS.

3.6. Thermokinetic analysis and estimation of activation energies of symmetrical and asymmetrical polysilanes

Figures 3(a)-3(c) represents non-isothermal T.G. curves of symmetrical/ asymmetrical polysilanes at different heating rates of 4, 8, and 12°C/min under argon atmosphere. From TG curves, it was observed that all the polysilanes exhibits only a single mass loss stage. With an increase in the heating rate, the mass loss stages of three polysilanes shifted to higher degradation temperatures because of heat transfer limitations. At a lower heating rate, the sample will take a higher amount of time to reach equilibrium because of the larger amount of instantaneous thermal energy is provided to the system. Whereas at higher reaction rates in the same temperature region, the system will have a shorter reaction time, and the sample requires a higher temperature for the decomposition process to compensate for the reduction in time. Thus, it can be concluded that the thermal degradation of polysilanes strongly depends on the heating rate. Thermal degradation, thermal stability, the kinetics of the degradation process, and the mechanism of degradation can be thoroughly explained by using kinetic methods. The kinetic analysis mainly deals with the measurement of process rates. The basic kinetic equation can be expressed in terms of the degree of conversion (α) and absolute temperature (T), as shown in Eq. (1).

$$\frac{d\varvec{\alpha}}{dt} = k(T)f(\varvec{\alpha})$$

1

Where f(α) is a reaction model, and k(T) is the reaction rate constant which can be illustrated by using the Arrhenius equation as follows

$$\mathrm{k(T)} = \mathrm{Aexp}\left(-\frac{\mathrm{E}_{\varvec{\alpha}}}{\mathrm{RT}}\right)$$

2

Where A is the pre-exponential factor, E_{α} is the activation energy in kJ/mol, R is the universal gas constant, and T is the absolute temperature. By substituting Eq. (2) in Eq. (1), the resultant equation can be expressed as:

$$\frac{\mathrm{d}\varvec{\alpha}}{\mathrm{dt}} = \mathrm{Aexp}\left(-\frac{\mathrm{E}_{\varvec{\alpha}}}{\mathrm{RT}}\right)\mathrm{f}(\varvec{\alpha})$$

3

Eq. (3) is the basic comparison for different kinetic methods, and it applies to both isothermal and non-isothermal heating conditions. At a given heating rate (β), for non-isothermal conditions, the basic kinetic equation can be rewritten as ;

$$\varvec{\beta}\frac{\mathrm{d}\varvec{\alpha}}{\mathrm{dt}} = \mathrm{Aexp}\left(-\frac{\mathrm{E}_{\varvec{\alpha}}}{\mathrm{RT}}\right)\mathrm{f}(\varvec{\alpha})$$

4

Unlike model-fitting methods, model-free methods are more impeccable and don't require any preceding information about the reaction model for the determination of E_{α}. As indicated by the ICTAC, the single heating rate is highly unreliable, and it tends to give un-accurate kinetic parameters, whereas, on the other hand, a multi-heating rate method gives meaningful values of activation energy. To analyze T.G. data, the most common methods used are isoconversional methods. Therefore, in the present study, frequently used multi-heating rate kinetic methods such as Ozawa and modified KAS methods were employed to determine the kinetic parameters of symmetrical/asymmetrical polysilanes by using T.G. analysis. For performing kinetic analysis, the degree of conversion (α) has to be determined from T.G. data. The degree of conversion is defined as the ratio of actual weight loss to total weight loss at a given step of the decomposition, and the same should be plotted against temperature at different heating rates. The degree of conversion (α) can be mathematically represented by Eq. (5).

$$\varvec{\alpha} = \frac{\mathrm{m}_0 - \mathrm{m}_\mathrm{T}}{\mathrm{m}_0 - \mathrm{m}_\mathrm{f}}\mathrm{x}100\%$$

(5)

Where m_0, $m_{T,}$ and m_f are initial mass, mass at a given temperature, and final mass of the polymer samples during the degradation process, respectively. If we consider non-isothermal degradation process, m_0 is the initial mass of the polymer sample.

Isoconversional methods are classified into two types; they are integral and differential methods. The most common integral method, the Ozawa method by Flynn and Wall, as shown in Eq. (6) is a more accurate, simple, and useful method for the determination of activation energies for a given α.

$$\ln(\varvec{\beta}) = \text{const} -1.052 \left(\frac{E_{\varvec{\alpha}}}{RT}\right)$$

6

Where β is the heating rate, R is the universal gas constant, Tα is the absolute temperature at a given value of α and Eα is the activation energy. It can be determined by knowing the value of the slope obtained from the linear plots between ln (β) and (1/Tα) as shown in Figs. 6(a)-6(c).

Table 5

Comparison of activation energies of PDMS and PDPS using Ozawa method

α	**Line equation**	**r^2**	**E_α (kJ/mol)**	**α**	**Line equation**	**r^2**	**E_α (kJ/mol)**
PDMS				PDPS			
0.1	-9.944x + 20.40	0.991	82.55	0.1	-23.16x + 42.38	0.994	192.61
0.2	-9.282x + 18.40	0.983	77.17	0.2	-79.30x + 131.8	0.984	659.35
0.3	-9.433x + 18.13	0.975	78.43	0.3	-114.5x + 185.6	0.995	952.62
0.4	-13.01x + 23.58	0.989	108.17	0.4	-77.67x + 124.0	0.934	645.74
0.5	-19.24x + 33.16	0.999	159.98	0.5	-101.8x + 160.1	0.999	847.14
0.6	-32.12x + 52.96	0.981	267.04	0.6	-101.1x + 157.0	0.958	840.52
0.7	-55.26x + 88.13	0.996	459.47	0.7	-148.4x + 227.5	0.946	1234.15
0.8	-80.22x + 125.3	0.983	666.97	0.8	-186.1x + 282.2	0.936	1547.77
0.9	-111.3x + 170.5	0.985	925.61	0.9	-335.1x + 502.4	0.907	2786.49
Avg			313.93	Avg			1078.49

Table 6
Comparison of activation energies of PDMS and PMPS using Ozawa method

α	**Line equation**	**r^2**	**E_α (kJ/mol)**	**α**	**Line equation**	**r^2**	**E_α (kJ/mol)**
PDMS				PMPS			
0.1	-9.944x + 20.40	0.991	82.55	0.1	-8.816x + 16.46	0.970	73.30
0.2	-9.282x + 18.40	0.983	77.17	0.2	-12.07x + 21.08	0.958	100.34
0.3	-9.433x + 18.13	0.975	78.43	0.3	-16.90x + 28.30	0.977	140.54
0.4	-13.01x + 23.58	0.989	108.17	0.4	-22.81x + 37.17	0.972	189.71
0.5	-19.24x + 33.16	0.999	159.98	0.5	-29.60x + 47.26	0.987	246.15
0.6	-32.12x + 52.96	0.981	267.04	0.6	-37.33x + 58.67	0.996	310.43
0.7	-55.26x + 88.13	0.996	459.47	0.7	-53.70x + 83.04	0.998	446.47
0.8	-80.22x + 125.3	0.983	666.97	0.8	-91.00x + 138.6	0.988	756.59
0.9	-111.3x + 170.5	0.985	925.61	0.9	-178.3x + 267.9	0.998	1482.54
Avg			313.93	Avg			416.22

Another useful and important method is the KAS method, which can be mathematically represented, as shown in Eq. (7).

$$\ln\left(\frac{\varvec{\beta}_i}{T^{1.92}_{\varvec{\alpha},i}}\right) = \text{const -1.0008}\left(\frac{E_{\varvec{\alpha}}}{RT}\right)$$

7

Where R is the universal gas constant, β_i is the heating rate expressed in K/min, $T_{\alpha,i}$ is the absolute temperature in K at the same value of α at different heating rates. E_α is the activation energy (kJ/mol) at a given value of α, and it can be determined from the slope of the linear plots of ln $(\beta/T^{1.92})$ v/s $1/T_\alpha$ as shown in Figs. 7(a) -7(c).

Tables 7 & 8 show the dependency of Eα as a function of α in modified KAS method. Even though there is a slight difference in the average values of activation energies obtained from this method compared to the Ozawa method, similar trends were observed for three polysilanes as compared to that of Ozawa's approach. An anomalous behavior was found in the value of Eα concerning α, and the highest activation energy was seen in the case of PDPS, which indicates that the degradation mechanism is very much complex when compared to that of PDMS and PMPS.

Table 7

Comparison of activation energies of PDMS and PDPS using modified KAS method

α	Line equation	r^2	$E_α$ (kJ/mol)	α	Line equation	r^2	$E_α$ (kJ/mol)
PDMS				PDPS			
0.1	-8.898x + 6.385	0.989	73.92	0.1	-22.06x + 28.27	0.994	183.46
0.2	-8.204x + 4.333	0.979	68.15	0.2	-78.13x + 117.5	0.984	649.61
0.3	-8.320x + 3.995	0.969	69.11	0.3	-113.3x + 171.4	0.995	942.66
0.4	-12.01x + 9.641	0.987	99.81	0.4	-76.45x + 109.7	0.932	635.60
0.5	-18.06x + 18.90	0.999	150.03	0.5	-100.6x + 145.8	0.999	836.86
0.6	-30.91x + 38.66	0.979	256.98	0.6	-99.84x + 142.7	0.957	830.11
0.7	-54.03x + 73.80	0.996	448.88	0.7	-147.1x + 213.1	0.945	1223.65
0.8	-78.97x + 110.9	0.983	656.06	0.8	-184.8x + 267.8	0.935	1537.17
0.9	-110.0x + 156.1	0.984	914.34	0.9	-333.8x + 488	0.906	2775.80
Avg			304.14	Avg			1068.32

Table 8

Comparison of activation energies of PDMS and PMPS using modified KAS method

α	Line equation	r^2	$E_α$ (kJ/mol)	α	Line equation	r^2	$E_α$ (kJ/mol)
PDMS				PMPS			
0.1	-8.898x + 6.385	0.989	73.92	0.1	-7.647x + 2.234	0.960	63.52
0.2	-8.204x + 4.333	0.979	68.15	0.2	-10.85x + 6.778	0.948	90.20
0.3	-8.320x + 3.995	0.969	69.11	0.3	-15.67x + 13.96	0.973	130.18
0.4	-12.01x + 9.641	0.987	99.81	0.4	-21.57x + 22.82	0.969	179.22
0.5	-18.06x + 18.90	0.999	150.03	0.5	-28.35x + 32.89	0.986	235.53
0.6	-30.91x + 38.66	0.979	256.98	0.6	-36.07x + 44.29	0.995	299.68
0.7	-54.03x + 73.80	0.996	448.88	0.7	-52.43x + 68.65	0.998	435.55
0.8	-78.97x + 110.9	0.983	656.06	0.8	-86.31x + 119.0	0.982	717.08
0.9	-110.0x + 156.1	0.984	914.34	0.9	-177.0x + 253.5	0.998	1470.66
Avg			304.14	Avg			402.40

The average values of activation energy obtained from two different methods for a given polymer sample were almost similar to one another. Even though the values of activation energy derived from the Ozawa method are slightly higher than that of the modified KAS method, both the methods will provide accurate or efficient mathematical approaches for performing the kinetic analysis for the thermal degradation of PDMS, PMPS, and PDPS.

4. Conclusions

In conclusion, polysilanes containing functionally different groups such as methyl, phenyl, and a combination of methyl and phenyl groups were successfully synthesized. FT-IR results established the identification of intended functional groups in as-synthesized polysilanes, thereby confirming the structure and bonding in polysilanes. Elemental (CHNO) analyzer estimated the percentage by weight (wt.%) of each element present in polysilanes, and the empirical formula of PDMS, PDPS, and PMPS was found to be $SiC_{2.01}H_{6.25}$, $SiC_{12.50}H_{10.26}$, and $SiC_{6.45}H_{7.76}$, respectively. Thermal stability and degradation of functionally different polysilanes were investigated using thermogravimetric analyzer in the presence of nitrogen atmosphere. Of the three polysilanes, the thermal stability of PDPS was found to be high because of the presence of phenyl rings on either side of the Si atom. The kinetic parameters of Kumada thermal condensation of PDMS, PMPS, and PDPS was determined applying isoconversional methods. The average values of the activation energy obtained from Ozawa and modified KAS method were found to be in good agreement with each other, Thermal and kinetic data as obtained from above kinetic analysis could be used beneficially to design the experiments for the preparation of polycarbosilane variants from these symmetrical and asymmetrical polysilanes.

Declarations

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors Contributions

All authors contributed to the study conception and design of experiment, polymer synthesis experiments, sample preparation for thermal and spectral characterization, data collection [Shahnawaz, M. and Ramcharan,T] The first draft of the manuscript was written by G Santhana Krishnan and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Ethics approval : All authors granted ethics approval

Consent to participate : We give our consent participate

Consent for publication : All the authors are giving consent to publish.

Availability of data and materials : No associated data

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Scheme

Scheme 1 & 2 are available in Supplementary Files section.

Figures

Figure 1

FT-IR spectra of (a) PDMS (b) PDPS (c) PMPS

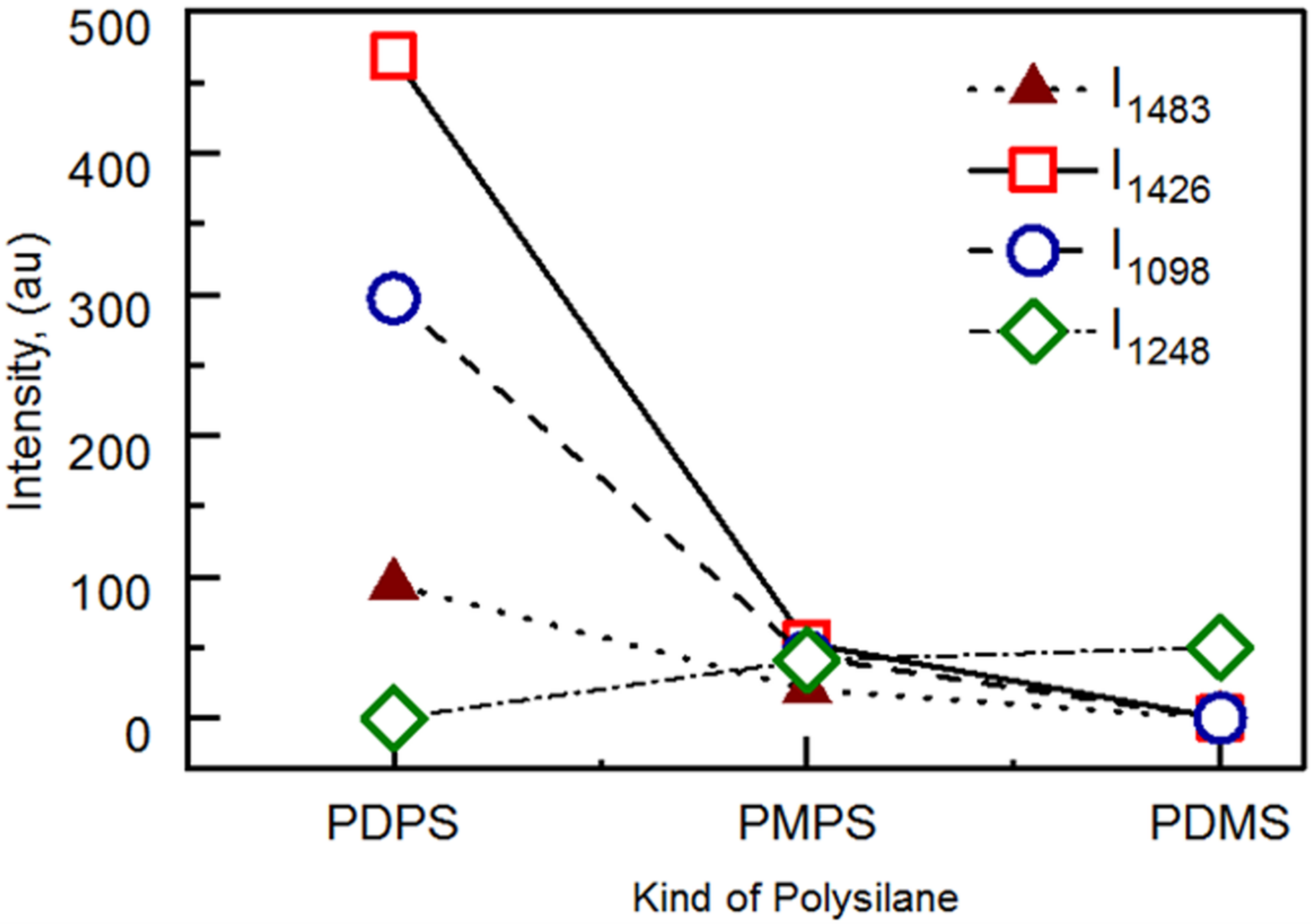

Figure 2

Comparison of different peak intensities of symmetrical/asymmetrical polysilanes

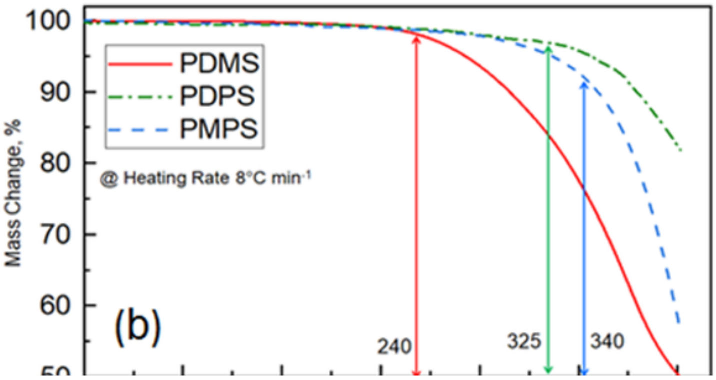

Figure 3

TG curves of symmetrical/asymmetrical polysilanes at (a) 4°C/min (b) 8°C/min and (c) 12°C/min

Figure 4

DSC Exotherms of (a) PMPS, (b) PDPS and (c) PDMS at a heating rate of 8°C/min

Figure 5

Plots of the degree of conversion (α) v/s temperature at different heating rates of (a) PDMS (b) PDPS (c) PMPS

Figure 6

Ozawa plots of (a) PDMS (b) PDPS (c) PMPS

Figure 7

Modified KAS plots of (a) PDMS (b) PDPS (c) PMPS

Supplementary Files

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- Scheme1.tif
- Scheme2.tif