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FACILE SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF TRIAZINE BASED DENDRIMER

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ABSTRACT

Hydroxyl terminated triazine based dendrimers were synthesized up to generation 2 using *N,N'*-bis(4,6-dichloro-1,3,5-triazin-2-yl)butane-1,4-diamine as core by divergent method. Core and half generation dendrimer (G1.5) were chlorine terminated and full generation dendrimers (G1) and (G2) were hydroxyl terminated. Synthesized dendrimer generations were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, ESI-Mass spectrometry and elemental analysis. Intrinsic viscosities of full generation dendrimer G1 and G2 were determined and hydrodynamic radii were calculated. Thermal properties of full generation dendrimers were investigated by thermo gravimetric analysis. Doyle's method was applied for evaluation of thermogravimetric data. Glass transition temperatures of dendrimer generations were determined by differential scanning calorimetry.

Key words: Dendrimer, Triazine trichloride, Diethanolamine, Thermo gravimetric Analysis, Integral procedural decomposition temperature.

INTRODUCTION

Dendrimers are defined as monodisperse macromolecules with perfectly branched regular structure and having at least one branched junction at each repeat unit[1]. Compared to linear polymers, dendrimers are monodisperse, nanosized and possess high terminal functionality and internal cavities, which displayed their candidature for many applications such as drug delivery[2], sensors[3], cancer therapy[4], MRI contrast agents[5], photodynamic therapy[6] and catalysis[7].

Mostly, dendrimers are difficult to synthesize as in the many cases, synthesis requires altercation of growth reaction, activation/deactivation or interconversion of

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functional groups and also complex isolation and purification of products so, efficient synthetic procedure is highly required[8]. Triazine trichloride derivatives are known for long periods of time[9] utilized in many applications ranging from pharmaceuticals to surfactants[10,11]. Several researchers have used triazine trichloride in dendrimer architecture as chlorine atoms of triazine trichloride can be substituted in temperature dependent manner and triazine trichloride is selective towards different amines[12-15]. Therefore dendrimer can be efficiently synthesized without using activation/deactivations of functional group and complex isolation procedures.

Thermal properties are important properties of any polymer. A handful reports are existing on thermal properties on pure dendrimer and most of them are on polyamidoamine type dendrimers[16-19]. A few groups have reported thermal properties of triazine based dendrimer hereinto, Lin et al.[20] reported thermal stability of triazine based dendritic molecules with diethanolamine and ethanolamine linkages on periphery limited to lower generations. Singh and Gupta[21] reported thermal stability of triazine based dendrimer with triazine trichloride as core and ester linkages on periphery. Didehban et al.[22] reported thermal properties of 4-bromo-(4-alkyloxybiphenyl-4'-Oxy) butane modified triazine dendrimer as liquid crystals and studied the effect of spacer length on thermal properties.

We have synthesized triazine based dendrimer up to generation 2 using *N, N'*-bis (4,6-dichloro-1,3,5-triazin-2-yl) butane-1,4-diamine as core. *N,N'*-bis(4,6-dichloro-1,3,5-triazin-2-yl)butane-1,4-diamine in first step using triazine trichloride and butane1,4-diamine as starting materials[20]. Dendrimer was then grown up to generation 2 using triazine trichloride and diethanolamine as linkers[22,23]. Synthesized dendrimer was characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, ESI-Mass spectrometry and elemental analysis. Hydrodynamic radius of the synthesized dendrimer generations were determined by intrinsic viscosity[24]. Thermal behaviors of full generation dendrimers were determined by thermo gravimetric analysis and differential scanning calorimetry.

EXPERIMENTAL

Materials and methods

Triazine trichloride (cyanuric chloride), butane-1,4 diamine, acetone, dichloromethane (DCM) and methanol were purchased from Sigma-Aldrich Ltd. Sodium hydroxide was purchased from Merck Ltd. All the reagents and solvents for the synthesis and analysis were used as received. FTIR studies were carried out in the range of 250-4000 cm^{-1} using Perkin-Elmer Spectrum RX-FTIR spectrometer instrument through KBr disc and pellet method or nujol mull method. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 MHz in

Brucker Avance II 400 (Germany) using TMS as internal standard. Mass spectra were recorded on Waters Micromass Q-ToF Micro (USA) instrument equipped with electrospray ionization. Elemental analysis recorded on Perkin-Elmer 2400 CHN elemental analyzer. Intrinsic viscosity was determined by using Ubbelohde viscosity measurement at 25°C in water solution. Thermogravimetric analysis was performed on Mettler Toledo TGA (Switzerland) instrument in a nitrogen atmosphere and heating rate was maintained at 10°C/min. Differential scanning calorimetry was performed on the Mettler Toledo DSC instrument in a nitrogen atmosphere and heating rate was maintained at 10°C/min.

Synthesis

Synthesis of N,N'-bis(4,6-dichloro-1,3,5-triazin-2-yl)butane-1,4-diamine (Core)

Cyanuric Chloride (0.02 mmol) was dissolved in dichloromethane and kept in an ice bath. A solution of butane-1,4-diamine (0.01 mmol) containing sodium hydroxide (0.02 mmol) in water was added drop wise in the solution of cyanuric chloride at 0-5°C with stirring. The solution was stirred at 0-5°C for 2 hrs. Then the solution was filtered, washed with methanol and acetone and dried under vacuum: A white colored solid was formed. Yield: 75%.

FT-IR (KBr, cm^{-1}) *v*: 3268 (NH), 2860, 2780 (Aliphatic C-H), 1721, 1620 (C=N of triazine), 846, 797 (C-Cl); ^{1}H-NMR (400 MHz, DMSO-d_6, δ): 1.5483-1.6603 (m, 4H, N-CH_2), 3.2929-3.3010 (m, 4H, N-CH_2); ^{13}C-NMR (75 MHz, DMSO-d_6, δ): 25.27, 25.71 (CH_2), 40.22, 40.88 (N-CH_2), 165.10, 169.46 (Triazine part); Anal. Calced for $C_{10}H_{10}Cl_4N_8$: C, 31.27; H, 2.62; N, 29.18 found C, 31.35; H, 2.66; N, 29.20.

Synthesis of generation 1 dendrimer (G1)

N,N'-bis(4,6-dichloro-1,3,5-triazin-2-yl)butane-1,4-diamine (0.01 mmol) was dissolved in an excess of diethanolamine (0.04 mmol), which was used as both solvent and reactant. The resulting mixture was refluxed for 2 hrs. After cooling, it was dispersed and washed by acetone repeatedly to give generation 1 dendrimer, which was light brown colored with honey like consistency. Yeild: 78%.

FT-IR (Nujol, cm^{-1}) *v*: 3363 (O-H), 2967 (aliphatic C-H), 1667 (C=N of triazine), 1064 (C-O); ^{1}H-NMR (400 MHz, D_2O, δ): 1.5433-1.5770 (m, 4H, CH_2), 3.2929-3.3010 (m, 4H, N-CH_2-), 3.5600-3.6293 (m, 16H, N-CH_2-CH_2-OH), 3.8873-3.9418 (m, 16H, N-CH_2-CH_2-OH); ^{13}C-NMR (75 MHz, D_2O δ): 25.22, 25.55 (CH_2), 40.25, 40.88 (N-CH_2), 57.04 (N-CH_2-CH_2-OH), 61.50 (N-CH_2-CH_2-OH), 165.11, 169.45 (triazine part); Anal. Calcd for $C_{26}H_{50}N_{12}O_8$: C, 47.40; H, 7.65; N, 25.52; Found C, 47.65; H, 7.70; N, 25.55.

Synthesis of generation 1.5 dendrimer (G 1.5)

Cyanuric chloride (0.08 mmol) was dissolved in dichloromethane and kept in an ice bath. A solution of G1 dendrimer (0.01 mmol) containing sodium hydroxide (0.08 mmol) in water was added drop wise in the solution of cyanuric chloride at 0-5°C with stirring. The solution was stirred at 0-5°C for 2 hrs and refluxed for 6 hrs. Then the solution was filtered, washed with methanol and acetone and dried under vacuum: A white colored solid was formed. Yield: 75%.

FT-IR (KBr, cm^{-1}): 3445 (N-H), 2781 (Aliphatic C-H), 1777, 1753, 1722 (C=N of triazine), 1053 (C-O), 772 (C-Cl); ^{1}H-NMR (400 MHz, DMSO-d_6, δ): 1.5433-1.5770 (m, 4H, CH_2), 3.2929-3.3010 (m, 4H, N-CH_2), 4.0529-4.1151 (m, 16H, N-CH_2-CH_2-O-), 4.1925-4.2311 (m, 16H, N-CH_2-CH_2-O-); ^{13}C-NMR (75 MHz, DMSO-d_6, δ): 25.29 (CH_2), 48.80 (N-CH_2), 57.10 (N-CH_2-CH_2-O-), 61.59 (N-CH_2-CH_2-O-), 163.37, 167.41, 17043, 172.46 (triazine part); Anal. Calcd for. $C_{50}H_{42}Cl_{16}N_{36}O_8$: C, 32.60; H, 2.30; N, 27.37; Found: C, 32.68; H, 2.36; N, 27.40.

Synthesis of generation 2 dendrimer (G2)

Generation 1.5 dendrimer (0.01 mmol) was dissolved in an excess of diethanolamine (0.16 mmol), which was used as both solvent and reactant. The resulting mixture was refluxed for 2 hrs. After cooling, it was dispersed and washed by acetone repeatedly to give generation 2 dendrimer, which was light brown colored with honey like consistency. Yield: 78%.

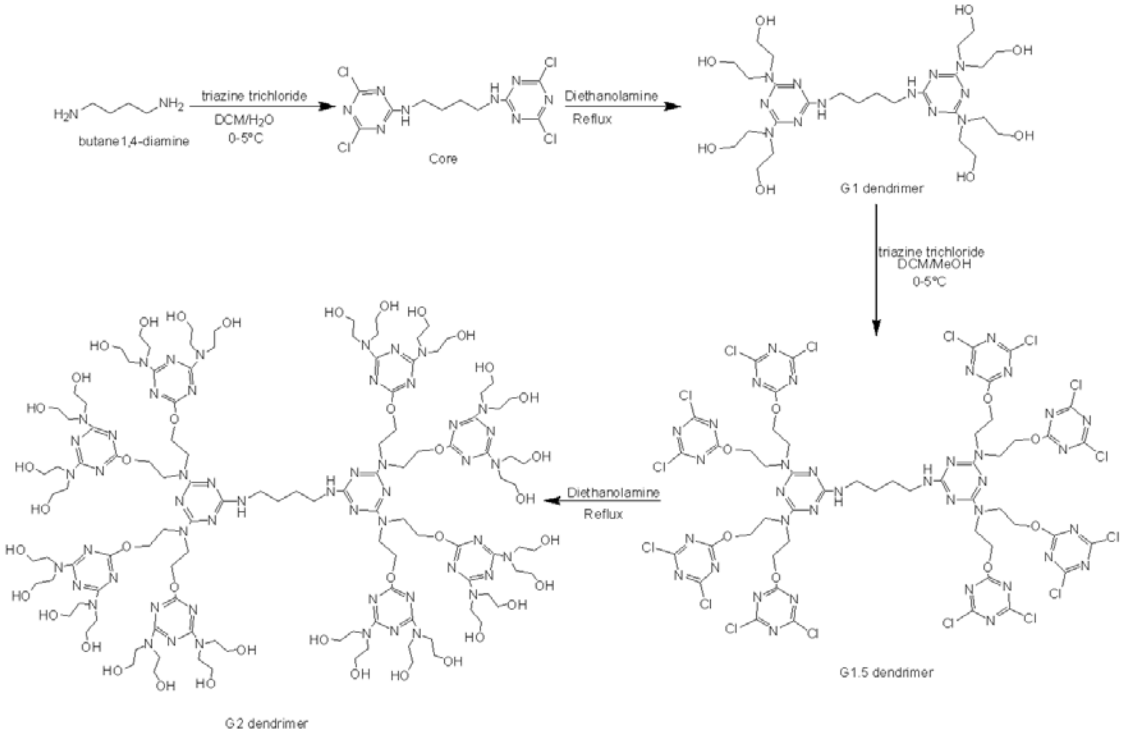
FT-IR (Nujol, cm^{-1}): 3356 (O-H), 2942, 2881, 2831 (aliphatic C-H), 1681, 1619 (C=N of triazine), 1071 (C-O); ^{1}H-NMR (400 MHz, D_2O, δ): 1.5725-1.5931 (m, 4H, CH_2), 3.1957-3.2220 (m, 4H, N-CH_2), 3.5817-3.6720 (m, 64H, N-CH_2-CH_2-OH), 3.7276-3.8027 (m, 64H, N-CH_2-CH_2-OH), 3.9002-3.9890 (m, 16H, N-CH_2-CH_2-O-), 4.0522-4.1272 (m, 16H, N-CH_2-CH_2-O-); ^{13}C-NMR (75 MHz, D_2O, δ): 25.12 (CH_2), 48.08 (N-CH_2), 55.54 (N-CH_2-CH_2-O-tri), 57.60 (N-CH_2-**C**H_2-OH), 59.87 (N-CH_2-CH_2-Otri), 61.51 (N-CH_2-CH_2-OH), 163.01, 163.08-164.68, 170.99-172.46, 177.47 (Triazine part); Anal. Calcd for $C_{115}H_{202}N_{52}O_{40}$: C 46.55, H 6.92, N 24.76; Found C 46.59, H 6.99, N 24.80. ESI-MS: Calcd molecular weight: 2942 Daltons, Obtained: 2943.3 (m/z).

RESULTS AND DISCUSSION

Synthesis

A hydroxyl terminated triazine based dendrimer was synthesized from *N,N'*-bis(4,6-dichloro-1,3,5-triazin-2-yl)butane-1,4-diamine as core. We exploited temperature controlled nucleophillic substitution of chlorine atoms of triazine trichloride. Selectivity of triazine trichloride towards secondary amine to hydroxyl group was also exploited. First chlorine atom of two moles of triazine trichloride was swapped by a mole of butane 1,4-diamine to give core for dendrimer synthesis[20]. Unreacted cyanuric chloride and butane 1,4-diamine both were easily removed from the reaction mass by washing with acetone and methanol respectively as the core was insoluble in both solvents. Second and third chlorine atoms were replaced by diethanolamine by as secondary amine of diethanolamine is more reactive than hydroxyl group[22-23].

The hydroxyl terminated triazine based dendrimer was dispersed and washed with acetone to remove unreacted diethanolamine. The hydroxyl groups of generation 1 dendrimer was again reacted with triazine trichloride to form chlorine terminated generation 1.5, which was again reacted with diethanolamine to give generation 2. Hydroxyl terminated dendrimer was prepared with low cost materials in high yields without involving any functional group manipulations and protection/deprotection strategies. Various generations of dendrimers were purified by washing and dispersing in solvents.



Scheme 1: Synthesis of triazine based dendrimer

Characterization

The growth of dendrimers was preliminary detected by solubility and appearance. The hydroxyl terminated full generation G1 and G2 dendrimers were soluble in water whereas chlorine terminated core and G 1.5 dendrimers were insoluble in water. Full generation dendrimer G1 and G2 were brown viscous liquids whereas core and G1.5 dendrimers were white solids.

Table 1: Physical description of dendrimer generations

Compound	Molecular formula	Appearance	Solubility in water	Surface groups (number)
Core	$C_{10}H_{10}Cl_{4}N_{8}$	White solid	Insoluble	Cl (4)
G1	$C_{26}H_{50}N_{12}O_{8}$	Brown liquid	Soluble	OH (8)
G1.5	$C_{50}H_{42}Cl_{16}N_{36}O_{8}$	White solid	Insoluble	Cl(16)
G 2	$C_{114}H_{202}N_{52}O_{40}$	Brown liquid	Soluble	OH(32)

Table 2: FT-IR absorption bands (cm^{-1}) for core and different generation of dendrimers

Compound	O-H	C-Cl	C=N	C-O
Core	---	797	1620	---
G1	3363	---	1667	1064
G1.5	---	772	1722	1053
G2	3356	---	1681	1071

The full generation G1 and G2 dendrimers were terminated by hydroxyl groups on the periphery whereas core and G1.5 half generation dendrimer were terminated by chlorine groups on the periphery. As shown in Table 2, the infrared spectrum shows the O-H stretching frequency at 3363 cm^{-1} and 3356 cm^{-1}, respectively, for G1 and G2 dendrimers, whereas C-Cl stretching was not detected, which was evident of hydroxyl groups on their periphery. Infrared spectrum shows C-Cl stretching frequency at 797 cm^{-1} and 772 cm^{-1}, respectively, for Core and G1.5 dendrimers, whereas O-H stretching remains undetected because of chlorine groups on their periphery. Also C-O stretching frequency was present in G1, G 1.5 and G2 at 1064 cm^{-1}, 1053 cm^{-1} and 1071 cm^{-1}, respectively, due to the presence of either ether linkage or hydroxyl group whereas C-O stretching frequency remains absent in the core.

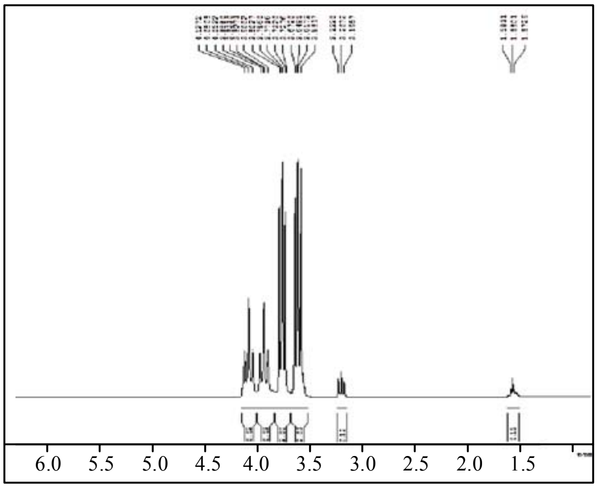


Fig. 1: ^{1}H-NMR spectra of generation 2 dendrimer

Structures of dendrimer generations were confirmed by ^{1}H-NMR. ^{1}H-NMR spectrum of core showed two multiplet at δ 1.5583-1.6603 and δ 3.2929-3.3010 ppm values, which corresponds to adjacent methyl groups in butane moiety. ^{1}H-NMR spectrums of G1, G1.5 and G2 dendrimers show multiplets in the region of δ 1.55-1.60 and δ 3.30-3.35 ppm regions, which showed butane moiety in each generation of the dendrimer. ^{1}H-NMR spectrum of G1 dendrimer showed additional triplets at δ 3.5600-3.6293 and δ 3.8873-3.9418 ppm values corresponds to two methylene protons in diethanolamine linkage as both methylene groups were in different environments. The hydroxyl proton G1 was substituted by triazine trichloride to give G1.5 dendrimer, which was confirmed by a ^{1}H-NMR spectrum of G1.5, which showed two triplets of diethanolamine linkage in the downfield region at δ 4.0529-4.1151 and δ 4.1925-4.2311 ppm value as an environment of methylene proton changes. Fig. 1 shows ^{1}H-NMR spectrum of G2 dendrimer, which indicates four triplets for methylene groups of diethanolamine linkages as four methylene groups of inner and outer diethanolamine linkages were in four different environments.

^{13}C-NMR proved to be a valuable tool for confirming structures of dendrimer generations. ^{13}C-NMR spectrum of core showed peaks at δ 25.27, 25.51, 40.22 and 40.88 ppm for butane moiety and δ 165.10 and 169.46 ppm for triazine part in core. ^{13}C-NMR spectrum of G1 showed peaks at δ 25.22, 25.55, 40.25, 40.88 ppm for butane moiety, δ 165.11, 169.45 ppm for triazine part and additional peaks at δ 57.00 and 61.50 ppm for diethanolamine part. ^{13}C-NMR spectrum of G1.5 dendrimer showed peaks at δ 25.29, 40.80 ppm for butane moiety, δ 57.00, 61.59 ppm for diethanolamine part, δ 163.37, 167.41 ppm for inner triazine part and δ 170.43, 172.46 ppm for outer triazine part of the structure. Fig. 2

shows ^{13}C-NMR spectrum of G2 dendrimer. Peaks at δ 25.12, 40.88 ppm for butane moiety, δ 57.60, 61.51 ppm for the inner diethanolamine part, δ 55.54, 59.87 ppm for outer diethanolamine part and δ 163.88-164.68 ppm for inner triazine part and δ170. 99-172.41 ppm for the outer triazine part.

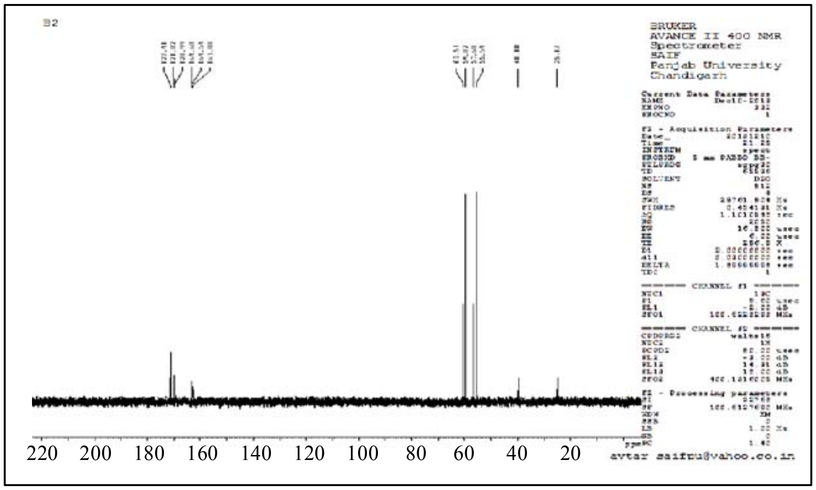


Fig. 2: ^{13}C-NMR spectrum of generation 2 dendrimer

Figure 3 shows ESI-Mass spectrum of G2 dendrimer. Calculated molecular weight was 2942 daltons for G2 dendrimer, obtained molecular weight was 2943.3 m/z value, which corresponds M+1 ion peak.

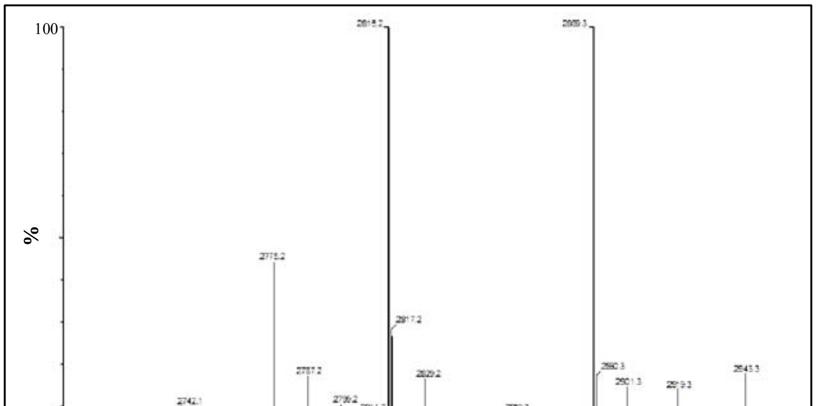


Fig. 3: ESI-Mass spectrum of G2 dendrimer

Elemental data of products are given in Table 3. All the calculated percentage matches theoretical percentages, which confirms their structures.

Table 3: Elemental data of synthesized dendrimers

Compound	Percentage of elements					
	Theoretical			Practical		
	C	H	N	C	H	N
Core	31.27	2.62	29.18	31.35	2.66	29.20
G1	47.40	7.65	25.52	47.65	7.70	25.55
G1.5	32.60	2.30	27.37	32.68	2.36	27.40
G 2	46.55	6.92	24.76	46.59	6.99	24.80

Intrinsic viscosity and hydrodynamic radius

In general, intrinsic viscosity of polymer was used to investigate interaction between polymer and solvent. Tomalia et al investigated hydrodynamic radius of dendrimer based on intrinsic viscosity measurement from below Hester-Mitchell relationship[24].

$$d = [240/\Pi \, N]^{1/3} \, [\eta \, M]^{1/3}$$

Intrinsic viscosities of full generation dendrimers were determined using water as solvent. From intrinsic viscosity, hydrodynamic radii of dendrimer generations were calculated. Results are displayed in Table 4. Generation 2 dendrimer showed higher hydrodynamic radii compared to generation 1 as number of terminal groups increases, which led to higher intrinsic viscosity and radii.

Table 4: Intrinsic viscosity and hydrodynamic radius of dendrimers at 25°C

Dendrimer with solvent	Molecular weight	Intrinsic viscosity (dl/g)	Hydrodynamic radius (°A)
G1 (H_2O)	658	0.032	6.92
G2 (H_2O)	2942	0.062	14.2

Thermal properties

Thermal properties of full generation dendrimers were evaluated by thermo gravimetric analysis. Fig. 4 (a and b) shows TGA graphs of G1 and G2 dendrimer. Both dendrimer, show two stage thermal decomposition behaviours. G1 dendrimer loses nearly 18% Wt. upto 150°C due to moisture. Between 200-450°C dendrimer was completely decomposed and left 4% residual wt. at 600°C. Similarly G2 dendrimer loses 17% wt. upto 150°C and decomposed completely between 150-500°C leaving 3% residual wt. at 600°C.

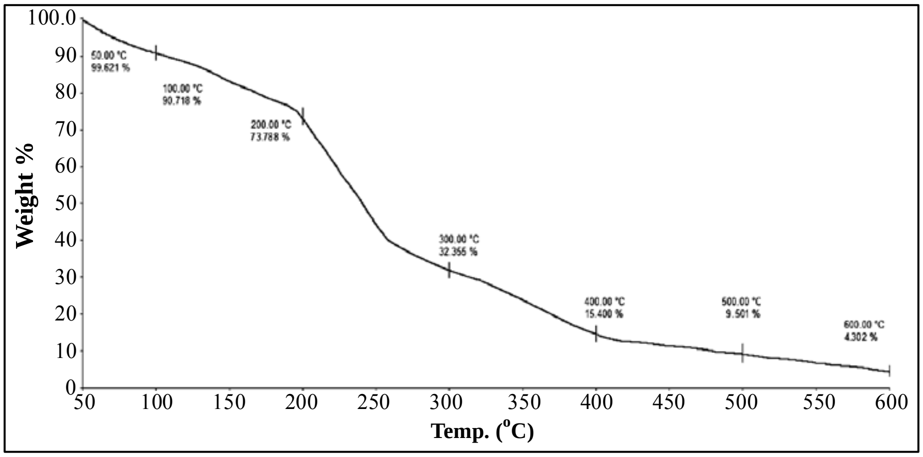


Fig. 4 (a): TGA graph of generation 1 (G1) dendrimer

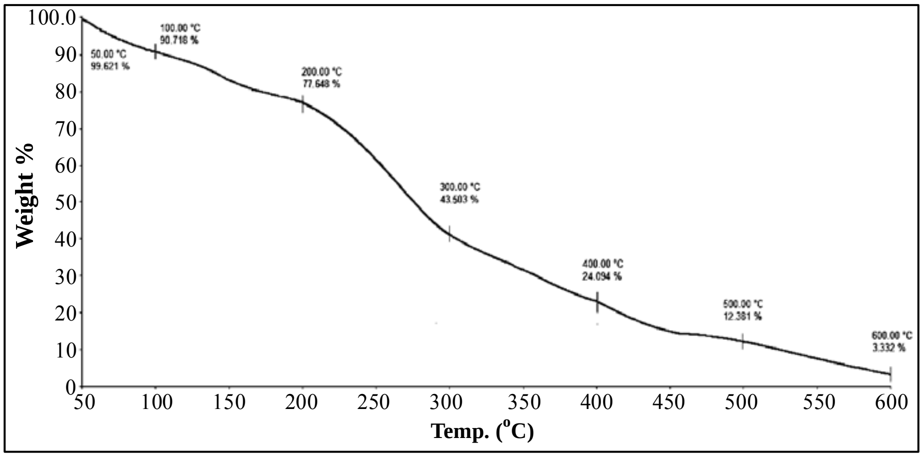


Fig. 4 (b): TGA graph of generation 2 (G2) dendrimer

Temperature for maximum rate of decomposition (T_{Max}) and temperature for 50% wt. loss ($T_{50\%}$) was determined for G1, G2 dendrimers furthermore, Integral procedural decomposition temperature (IPDT) was also determined by Doyle's method[25]. The results are displayed in Table 5. The results clearly indicate that G2 dendrimer has highest T_{max}, $T_{50\%}$ and IPDT.

Table 5: Characteristic temp. and thermal data for different generations of dendrimers

Products	% Wt. loss at different temperatures						Decomposition temp. range (°C)	T_{Max}[a] (°C)	$T_{50\%}$[b] (°C)	IPDT[c] (°C)
Temp. (°C)	100	200	300	400	500	600				
G1	10	26	68	85	91	97	150-400	250	240	260
G2	9	23	57	76	88	97	200-500	310	275	332

Glass transition temperature (Tg) of G1 and G2 dendrimers were determined by differential scanning calorimetry. Results are furnished in Table 6. G1 and G2 dendrimers have glass transition temperatures of -28.6 and -11.0, which was a typical for dendrimer[26]. Glass transition temperatures increases with increase in generation number as molecular weight increases.

Table 6: Dendrimer generations and glass transition temperatures

Generation	Glass transition temperature (°C)	
	On set	Mid-Point
G1	- 29	-28.6
G2	-12.0	-11.0

CONCLUSION

Hydroxyl terminated dendrimers were synthesized up to generation 2 using efficient synthetic route without using protection/deprotection or interconversion of functional group with easy purification. The synthesized dendrimers were characterized by spectral techniques. Intrinsic viscosity and hydrodynamic radii of full generation dendrimers G1 and G2 were 6.92 and 14.2 °A. G2 dendrimers shows highest thermal stability along with T_{max}, $T_{50\%}$ and IPDT. Glass transition temperatures (Tg) of G1 and G2 dendrimers were -28.6 and -11.0, respectively. Glass transition temperatures also increase with increase in generation number.

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