Synthesis, spectroscopic characterisation, electron microscopic study and thermogravimetric analysis of a phosphorus-containing dendrimer with phloroglucinol as a core unit

Echchukattula Dadapeer and Chamarthi Naga Raju*

Department of Chemistry, Sri Venkateswara University, Tirupati-517 502, India

A phosphorus-containing dendrimer of up to four generations with phloroglucinol as a core unit was synthesised using a divergent growth method. A repetitive synthetic sequence of several types of reactions was performed by using $P(O)Cl_3$, 3-hydroxybenzaldehyde, 4-hydroxybenzaldehyde and *p*-phenylenediamine for the synthesis of this dendritic molecule G_4 involving simple condensation reactions. This Schiff's base macromolecule possesses 12 imine bonds and 6-OH groups on the periphery. The structures of the intermediate generations G_1, G_2, G_3 were confirmed by IR, ^1H, ^{13}C, ^{31}P NMR and LC/EI MS. The final dendrimer G_4 was characterised by IR, ^1H, ^{13}C, ^{31}P NMR, Maldi-tof mass spectrometer and C, H, N analysis. The scanning electronic microscopic study and thermogravimetric analysis were also performed for the final dendrimer (G_4).

Keywords: phosphorus-containing dendrimer, divergent growth method, phloroglucinol, Schiff's base, scanning electron microscopy, thermogravimetric analysis

Well-defined, monodispersed macromolecules with uniform branched structures are called dendritic macromolecules. They constitute a ubiquitous type of precisely defined polymers,[1] potentially usable in numerous applications. Recently, there has been a growing interest in the synthesis of dendrimeric systems which offers the opportunity to generate monodisperse, structure-controlled macromolecular architectures similar to those observed in biological systems.[2] The phosphorus-containing dendrimers are useful for biological purposes.[3] The presence of phosphorus on the surface or within the cascade structure of dendrimers, or at the focal point of dendrons confers on phosphorus dendrimers fascinating properties.[4] Among other useful applications of phosphorus dendrimers, they can be used as hydrogels, hybrid organic–inorganic materials, nanolatex, nanotubes, microcapsules and fibres.[5] As much to the extent that a dendrimer possesses its own structure and molecular properties, identification of new monomers for dendrimer synthesis continues to be attractive. Thermo gravimetric analysis (TGA) is generally employed to determine characteristics of materials such as polymers and dendrimers, to determine degradation temperature, absorbed moisture content, *etc.* Simultaneous TGA-DTA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (*e.g.*, melting point) and those which involve a weight loss (*e.g.*, degradation). So thermal stability appears as an important point for the most applications of the dendrimers, and particularly in the field of materials science.[6] Scanning electron microscopy (SEM) gives the information about the sample's surface topography, composition, electrical conductivity, *etc.* SEM micrographs have a characteristic three-dimensional appearance useful for understanding the surface structure of the sample.

In our endeavour to synthesise a new type of dendrimer, we report here the synthesis of a phosphorus-containing dendrimer of four generations, with phloroglucinol 1,3,5-trihydroxybenzene as a core unit. Phloroglucinol was used previously by Chow and co-workers[7] as the branching unit of dendron derivatives. We have chosen alsothe symmetrically functionalised phloroglucinol as the core and have chosen $P(O)Cl_3$, 3-hydroxy benzaldehyde, 4-hydroxybenzaldehyde and *p*-phenylenediamine as branching components in the synthesis of the dendrimer. We have adopted a divergent growth method for the preparation of the dendritic molecule involving simple condensation reactions.

Results and discussion

Synthesis of the phosphorus-containing dendrimer (G_4) having phloroglucinol as a core unit is presented in Scheme 1. The first step of the synthesis was a condensation reaction of phloroglucinol (G_0) with $POCl_3$ in presence of triethylamine at –15 to 40 °C in dry THF with stirring for 2–3 h to afford the corresponding G_1. After filtration, G_1 was then treated with 3-hydroxy benzaldehyde in dry THF in presence of triethylamine at 40–45 °C with stirring for 4–5 h to form G_2. Then compound G_2 was reacted with *p*-phenylenediamine in refluxing dry EtOH to afford G_3. Finally the compound G_3 was treated with 4-hydroxybenzaldehyde in dry EtOH at reflux temperature for 5–6 h to afford the dendritic macromolecule G_4. As the size of the dendron increases the reaction becomes sluggish and the yield is low. To improve the yield of G_4, alcohol is taken in excess and the temperature is maintained at reflux with continued stirring for long periods. Scheme 1 sumarises the preparation of the dendrimer G_4 and the yield of the final dendrimer was a moderate 60%. The intermediates G_1, G_2, G_3 were characterised by IR, ^1H, ^{13}C, ^{31}P NMR and LC/EI mass spectrometry. The synthetic and analytical data of the dendrimer G_4 are given in the experimental section. The dendrimer G_4 exhibited absorption bands for –OH and P=O, in the regions 3368 and 1256 cm^{-1} respectively. P–O–$C_{(aromatic)}$ gave two absorptions in the regions 980 and 1192 cm^{-1}.[8,9] An absorption band for CH=N is observed at 1601 cm^{-1}. In the ^1H NMR spectra (500 MHz) of G_4, the aromatic protons gave multiplet in the region δ 6.57–7.79. The aromatic –OH protons resonated at δ 9.78 as a singlet. The CH=N protons gave chemical shifts in the region 8.45 and 8.51 in two environments. The ^{13}C NMR spectrum was recorded for G_4 and the data are given in the experimental part. The aromatic carbons resonated in the region 114.8–160.5 ppm and the $\underline{CH}$=N Carbon signal was observed at δ 163.8. G_4 gave a ^{31}P NMR signal[10] at δ –1.86. The dendrons G_1, G_2 and G_3 showed phosphorus –31 resonance signals in the expected regions and their data are given in the experimental section. The mass spectroscopic data of the final

Table 1 Mass data of G_4 obtained from MALDI

Dendrimer	Calculated mass	MALDI mass
G_4	2156.08	2156.00

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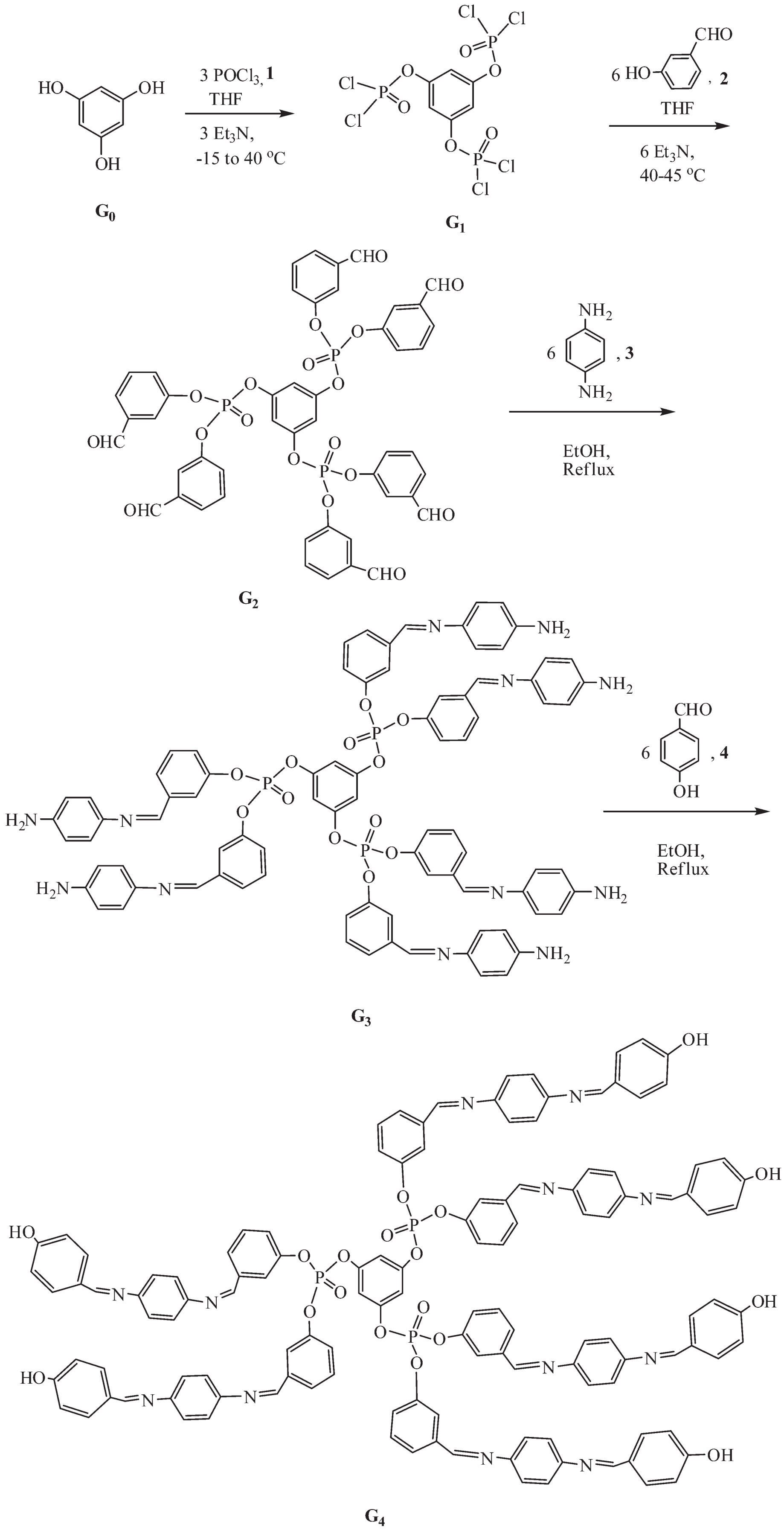
* Correspondent. E-mail: rajuchamarthi10@gmail.com


G0
3 POCl3, 1
THF
3 Et3N,
-15 to 40 °C
G1
6 HO–C6H4–CHO, 2
THF
6 Et3N,
40-45 °C
G2
6 NH2–C6H4–NH2, 3
EtOH,
Reflux
G3
6 CHO–C6H4–OH, 4
EtOH,
Reflux
G4

Scheme 1

dendrimer G_4 are determined by matrix assisted laser desorption /ionisation (MALDI) mass spectrometry. As expected, the mass obtained from the MALDI measurements corresponds closely to the calculated value.

The surface topography of the molecule was studied by SEM. The molecular decomposition of the dendrimer G_4 was investigated by TGA and DTA.

SEM

SEM images depict the surface structure of the dendritic material (G_4). In order to get a deeper insight into the properties of the surface of the C_6H_4–OH terminated dendritic macromolecular material, we have also carried out an SEM analysis. With increasing size it was clear that the overall surface morphology of the material tended to assume a nanoscale size gravel shape at a line width of 2 μm. Figure 1 shows the micrograph of the material with a line width of 10 μm and Fig. 2 shows the particle structure of the material with a line width of 2 μm.

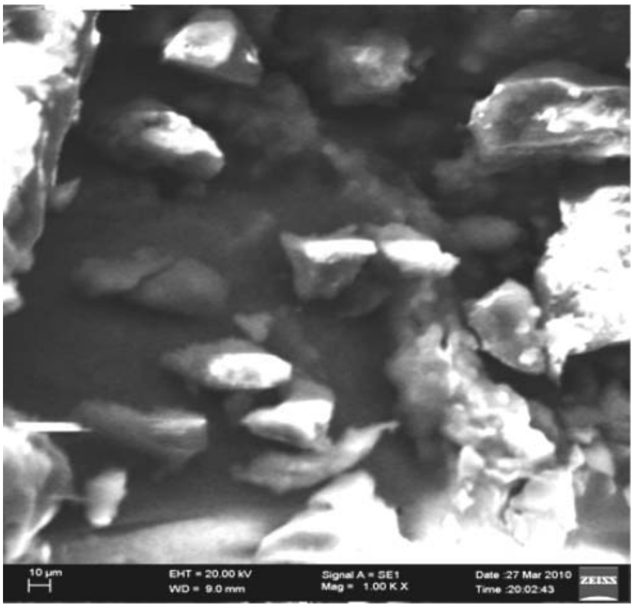


Fig. 1 SEM picture of the dendrimer G_4.

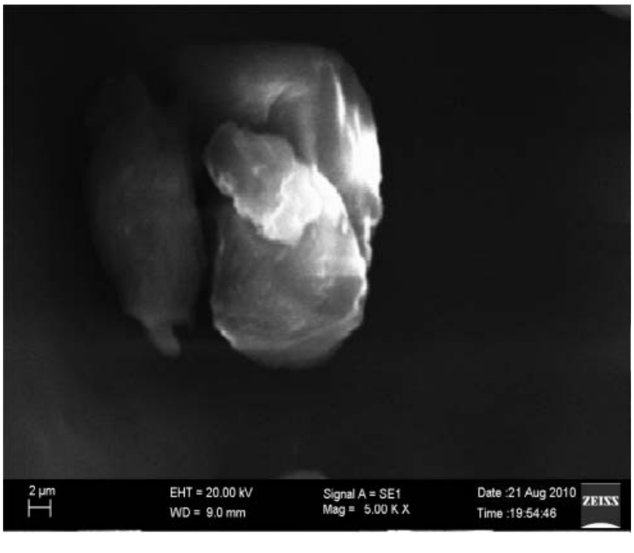


Fig. 2 Particle structure of G_4.

TGA-DTA

TGA was carried out on G_4 to determine changes in weight in relation to change in temperature. Similarly, DTA, a thermoanalytic technique was also carried out on G_4 to detect the changes in the sample, either exothermic or endothermic. Simultaneous TGA-DTA, which measures both heat flow and weight changes in a material as a function of temperature in a controlled air atmosphere was recorded. The TGA-DTA analysis of the compound was recorded up to 400 °C. The TGA graph shows that the compound is stable up to 85 °C and that minor decomposition starts at around 90 °C with a corresponding weight loss of approximately 5% water and continues up to 100 °C. The calculated water loss is 5.3%. Then the compound is stable up to 220 °C. Then a sudden decomposition starts at 220 °C with an observed weight loss of approximately 58% and this continues up to around 400 °C. A stable product of the compound is indicated by the constant weight in the plateau of the thermogram (100–200 °C). An overlay of TGA and DTA plots for the test compound (G_4) up to 400 °C is shown in Fig. 2. From the DTA curve, the heat of reaction was calculated. The DTA profile (Fig. 3) shows an endotherm peak at 95 °C corresponding to the loss of water and an endotherm at 45 °C, corresponding perhaps to the loss of a small branch. The exotherm at 220 °C seems to be due to a major degradation of the dendrimer structure.

Experimental

All the reagents used in this study were purchased from Sigma-Aldrich Chemical Company and used without further purification. THF and EtOH were dried by standard methods. TLC was performed on precoated plates with silica gel $60F_{254}$ (Merk).Column chromatography was performed on silica gel (0.040–0.063 mm, Macherey Nagel).The melting points were determined on a Buchi R-535 (Flawil, Switzerland) melting point apparatus and are uncorrected. IR Spectra were recorded on JASCO Japan FT IR-5300 spectrometer at the University of Hyderabad using KBr optics.^{1}H and ^{13}C NMR spectra of G_4 were recorded on a Bruker A VIII 500 MHz NMR spectrometer at IIT, Chennai, operating at 500.13 MHz for ^{1}H, and 125.75 MHz for ^{13}C NMR; data were recorded in the solvent DMSO-d_6 and chemical shifts were referenced to TMS (^{1}H and ^{13}C). ^{1}H and ^{13}C NMR spectra of G_1, G_2 and G_3 were recorded on a Bruker A VIII 400 MHz NMR spectrometer at Laila Impex, Vizayawada, operating at 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C NMR; data were recorded in the solvent DMSO-d_6 and chemical shifts were referenced to TMS (^{1}H and ^{13}C). ^{31}P NMR were recorded on a Bruker ACF Supercon 200 spectrometer operating at 81 MHz at the University of Hyderabad, Hyderabad. ^{31}P NMR data were recorded in the solvent $CDCl_3$ or DMSO-d$_6$ and chemical shifts were referenced to 85% H_3PO_4. EI mass spectra of intermediate dendrons G_1, G_2 and G_3 were recorded on a JEOL GCmate at IIT, Chennai and for mass chromatogram, LC Mass spectra of intermediate dendrons G_1, G_2 and G_3 were recorded on LCMS-2010A Shimadzu, spectrometer at University of Hyderabad, Hyderabad. The MALDI mass spectrum of the final dendrimer G_4 was recorded using a Applied Biosystems MALDI-TOF Voyger depro spectrometer. The sample was run using Sinapic acid as the matrix with DMSO as the solvent in the dried-droplet preparation method, performed at IIT, Madras, Chennai. TGA-DTA measurement was taken using a SDT Q600 V8.2 built instrument, performed at IISc, Bangalore. SEM images were taken with a Carl Zeiss, EVO MA15 Instrument. SEM operated at 20 kV, performed at Department of Physics, S. V. University, Tirupati, India. Elemental analyses were performed using EA 1112 Thermo Finnigan instrument, France, at University of Hyderabad, Hyderabad, India.

Preparation of G_1: A solution of $POCl_3$ (1. 39 mL, 0.015 mol) **(1)** in 20 mL of dry THF was added dropwise over a period of 20 min to a mixture of stirred solution of phloroglucinol (G_0) (0.63g, 0.005 mol) in 25 mL of dry THF and triethylamine (2.08 mL, 0.015 mol) at –15 °C. After stirring for 3 h at 40 °C, formation of G_1 was ascertained by TLC analysis run in a 2:8 mixture of ethyl acetate and hexane and the average Rf value observed was 0.75. Triethylamine hydrochloride was removed by filtration. The filtrate (G_1) was used for the next reaction step without further purification. The compound

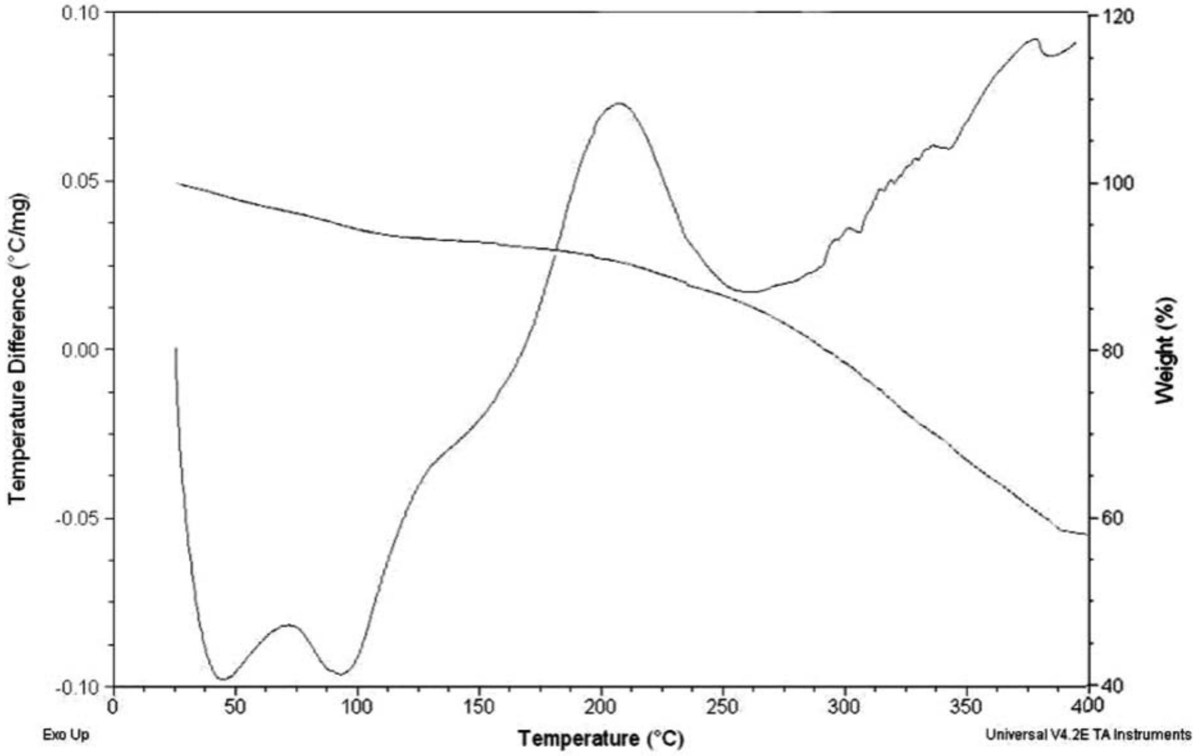


Fig. 3 TGA-DTA of the dendrimer G_4: top curve, DTA; lower curve, TGA.

(G_1) thus obtained was characterised by IR, ^{1}H, ^{13}C, ^{31}P NMR , LC/EI mass and C, H, N analysis. Yield 80%, υ_{max} (KBr, cm^{-1}): 1272 (P=O). ^{1}H (400 MHz, DMSO-d_6), 6.84(3H, s, ArH). ^{13}C (100 MHz, DMSO-d_6), 154.0 (C_0^1, C_0^3 and C_0^5), 96.5 (C_0^2, C_0^4 and C_0^6). ^{31}P NMR (81 MHz, $CDCl_3$). –0.35 ppm. EI MS: *m/z* 473.10 $[M]^{+\cdot}$, 475.00 $[M+2]^{+\cdot}$, 477.00 $[M+4]^{+\cdot}$. LC MS: *m/z* 473.00 $[M]^+$ 475.00 $[M+2]^{+\cdot}$, 477.00 $[M+4]^{+\cdot}$. Anal. Calcd for $C_6H_3Cl_6O_6P_3$: C, 15.12; H, 0.63. Found: C, 15.21; H, 0.68%.

Praparation of $G_{2:}$ To a mixture of stirred solution of the filtrate G_1 and triethylamine (4.5 mL, 0.03 mol), a solution of 3-hydroxybenzaldehyde **(2)** (3.66 g, 0.03 mol) in 25 mL of dry THF was added dropwise over a period of 20 min at 0–5 °C. After stirring for 4 h at 40–45 °C, formation of G_2 was ascertained by TLC analysis run in a 4:6 mixture of ethyl acetate and hexane and the average Rf value observed was 0.65.Triethylamine hydrochloride was removed by filtration. The solvent was evaporated under reduced pressure to obtain a crude product. This was purified by column chromatography eluting with ethyl acetate:hexane (2:8). The compound thus obtained was characterised by IR, ^{1}H, ^{13}C, ^{31}P NMR, LC/EI mass spectrometry and C, H, N analysis and used for the next reaction step. Yield 75%, υ_{max} (KBr, cm^{-1}): 1255 (P=O), 941, 1167 (P–O–$C_{aromatic}$), 1693 (Ar-CHO). ^{1}H (400 MHz, DMSO-d_6), 7.17–7.40 (27H, m, ArH), 9.91(6H, s, Ar-CHO). ^{13}C (100 MHz, DMSO-d_6), 153.9 (C_0^1, C_0^3 and C_0^5), 96.5 (C_0^2, C_0^4 and C_0^6), 149.01 (C_1^1),115.0 (C_1^2),137.6 (C_1^3), 120.6 (C_1^4),130.0 (C_1^5) 121.9 (C_1^6) and 193.0 (Ar-$\underline{C}$HO). ^{31}P (81 MHz, $CDCl_3$), –13.05 ppm. EI MS: *m/z* 991.15 $[M+H]^{+\cdot}$, LC MS: *m/z* 991.30 $(M+H)^{+}$. Anal. Calcd for $C_{48}H_{33}O_{18}P_3$: C, 58.19; H, 3.36. Found: C, 58.25; H, 3.31%.

Preparation of G_3: To a stirred solution of G_2 in 25 mL of dry EtOH, a solution of *p*-phenylenediamine **(3)** (3.24 g, 0.03 mol) in 25 mL of dry EtOH, was added at room temperature. After stirring for 5h at reflux temperature, formation of G_3 was ascertained by TLC analysis run in a 3:7 mixture of ethyl acetate and hexane and the average Rf value observed was 0.65. The solvent was evaporated under reduced pressure to get a crude product. This was purified by column chromatography eluting with ethyl acetate and hexane (3:7). The imine thus obtained was characterised by IR, ^{1}H, ^{13}C, ^{31}P NMR, LC/EI Mass and C, H, N analysis and used for the next reaction step. Yield 70%, υ_{max} (KBr, cm^{-1}): 1248 (P=O), 956, 1176 ((P–O–$C_{aromatic}$), 3217 str, 1450 bending (Ar-NH_2), 1622 (CH=N). ^{1}H (400 MHz, DMSO-d_6), 6.60–7.33 (51H, m, ArH), 8.51(6H, s, Ar-CH=N), 5.26 (12H, s, Ar-NH_2). ^{13}C (100 MHz, DMSO-d_6), 153.3 (C_0^1, C_0^3 and C_0^5), 96.3 (C_0^2, C_0^4 and C_0^6), 151.1 (C_1^1),114.1 (C_1^2),136.6 (C_1^3), 117.6 (C_1^4),129.3(C_1^5), 119.5 (C_1^6), 142. 6 (C_2^1),122.4 (C_2^2/ C_2^6),113.7 (C_2^3/ C_2^5), 148.0 (C_2^4) and 157.7 (Ar-$\underline{C}$H=N). ^{31}P (81 MHz, $CDCl_3$), –19.22 ppm. EI MS: *m/z* 1532.03 $(M+H)^+$, LC MS: *m/z* 1532.15 $(M+H)^{+}$**.** Anal. Calcd for $C_{84}H_{69}N_{12}O_{12}P_3$: C, 65.88; H, 4.54; N, 10.98%. Found: C, 65.71; H, 4.58; N, 10.86%.

Preparation of $G_{4:}$ To a stirred solution of G_3 in 30 mL of dry EtOH, a solution of 4-hydroxybenzaldehyde **(4)** (3.66 g, 0.03 mol) in 25 mL of dry EtOH, was added at room temperature. After stirring for 5h at reflux temperature, formation of G_4 was ascertained by TLC analysis run in a 4:6 mixture of ethyl acetate and hexane and the average Rf value observed was 0.35. The solvent was evaporated under reduced pressure to afford a crude product. This was purified by washing with ethyl acetate and hexane. Then G_4 was purified by column chromatography on silica gel (eluent: ethyl acetate) to afford a brown coloured powder in 60% yield. The imine thus obtained was characterised by IR, ^{1}H, ^{13}C, ^{31}P NMR, MALDI-TOF mass spectrometry and C, H, N analysis. Yield 60%, υ_{max} (KBr,cm^{-1}): 3368 (Ar-OH), 1256 (P=O), 980, 1192 (P–O–$C_{aromatic}$), 1601 (CH=N). ^{1}H (500 MHz, DMSO-d_6), 9.78 (6H, s, Ar-OH), 6.84–7.79 (75 H, m, ArH), 8.44, 8.51 (12H, s, –CH=N). ^{13}C (125 MHz, DMSO-d_6), 154.9 (C_0^1/ C_0^3/ C_0^5), 96.4 (C_0^2/ C_0^4/ C_0^6, 149.7 (C_1^1), 114.9 (C_1^2, 138.6(C_1^3, 120.1 (C_1^4), 130.3 (C_1^5), 122.2 (C_1^6, 147.4 (C_2^1/ C_2^4), 122.9 (C_2^2/ C_2^3/ C_2^5/ C_2^6, 128.8 (C_3^1), 131.1 (C_3^2/ C_3^6, 116.3 (C_3^3/ C_3^5), 160.5 (C_3^4), 163.8 (CH=N). ^{31}P (81 MHz, $CDCl_3$), –1.86 ppm. [MALDI-TOF]: *m/z* 2156.00 $[M+H]^+$. Anal. Calcd for $C_{126}H_{93}N_{12}O_{18}P_3$: C, 70.19; H, 4.35; N, 7.80%. Found: C, 70.10; H, 4.41; N, 7.85%.

Conclusion

The synthesis of a novel dendritic macromolecule G_4 has been accomplished. The condensation reactions were performed in dry tetrahydrofuran in the presence of triethylamine and the Schiff's base preparations were perfomed in dry ethanol. The deeper surface topography of the dendritic molecule G_4 was observed by SEM. This reveals a nano-sized gravel particle with a diameter of 2 μm. The thermal stability and changes in weight in relation to change in temperature and the heat of the final dendritic molecule G_4 were studied by TGA-DTA analysis. This reveals that the compound G_4 starts decomposition at

90 °C, due to loss of 5% of water molecules. Then the substance decomposes suddenly at 220 °C losing 58% by weight. The DTA curve reveals the heat change is endothermic for the loss of water and for the 58% decomposition of the compound the heat change is exothermic at around 220 °C. An endothermic peak at 45 °C is perhaps due to loss of water molecules and a small branch of G_4.

The authors express their thanks to HRDG, CSIR, New Delhi, India for sanctioning a major research project (01(2309)/09/EMR-II).

Received 17 June 2010; accepted 27 September 2010
Paper 1000208 doi: 10.3184/030823410X12887232916505

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