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REVIEW

Synthesis and thermal study of phosphorus containing dendron using 2-butyne-1,4-diol at the core

E. Dadapeer, K. Reddi Mohan Naidu, C. Naga Raju *

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

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2-Mercaptoethanol

Abstract Synthesis of new phosphorus dendron containing 2-butyne-1,4-diol at the core is described. The divergent build-up of the dendron is based on simple condensation reactions performed by using $P(O)Cl_3$, 3-hydroxybenzaldehyde, hydrazine hydrate, 4-hydroxybenzaldehyde and 2-mercaptoethanol. The final dendron is a Schiff's base macromolecule possessing 8 imine bonds and 8 OH groups at the periphery. The intermediate dendrons were confirmed by IR, NMR (^1H, ^{13}C and ^{31}P), LC–Mass and C, H, N analyzes. The structure of the final dendron **6** was confirmed by IR, NMR (^1H, ^{13}C and ^{31}P), MALDI-TOF-MS, and C, H, N analysis. The surface morphology of the dendron **6** was understood by Scanning Electronic Microscopic study (SEM). To determine the changes in weight in relation to change in temperature of the final dendron **6** was studied by TGA/DTA analysis.

Contents

* Corresponding author. Tel.: +91 9703193375.
E-mail address: rajuchamarthi10@gmail.com (C. Naga Raju).

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1. Introduction

The field of dendrimer chemistry (Zimmerman, 1999) has undergone a rapid development in establishing the synthetic approaches, characterization of dendrimer properties and design of functional dendrimers (Archut and Vögtle, 1998). The hyperbranched and monodispersed macromolecules which are commonly referred to as dendrimers are becoming important in efficient nanomaterials for a variety of applications in medicine, catalysis and electronics (Antoni et al., 2007). Nowadays development of chemistry of dendrimers is becoming an attractive field of research in nanosciences (Newkome and Shreiner, 2008). In general, they consist of core, branching structure and periphery. So, the physical and chemical properties and hence the applications of the dendrimers depend on the nature of these basic constituents. The dendrimers containing heteroatom occupy a relatively marginal place when compared to organic dendrimers, but a rich diversity of structures is available, particularly for phosphorus dendrimers and they possess interesting properties (Majoral and Caminade, 1999). The presence of phosphorus on the surface or within the cascade structure of dendrimer or at the focal point confers to phosphorus dendrimers fascinating properties. The very first example of phosphorus-containing dendrimer was polyphosphonium dendrimer (Rengan and Engel, 1990) and the first neutral phosphorus dendrimer was described by Launay et al. (1994). The phosphorus dendrimers possess interesting and unprecedented properties, which led to some potential applications from biology to material science (Majoral and Caminade, 2003). A few properties of P-dendrimers were highlighted by Caminade et al.(2010). A significant effort in the design and synthesis of these dendritic architectures has led to inside-out (divergent) or outside-in (convergent) methodologies (Washio et al., 2005). The synthetic elaboration and study of the properties of dumbbell-shaped dendrimers are much less explored when compared with globular dendrimers (Tatiana and Ashok, 2008). We have reported (Dadapeer et al., 2010) a novel linear phosphorus containing dendron using diphenylsilanediol at the core. In this paper we intrigued by the possibility of developing a dendron using 2-butyne-1,4-diol at the core giving rise to linear dumbbell-shape by using divergent method. We focus on scanning electron microscopic study to know in particular how the nanometric size property to be considered and thermogravimetric analysis to show the thermal stability and change in weight in relation to change in temperature for the final dendron **6**.

2. Experimental section

2.1. Materials and reagents

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 method. 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).

2.2. Instruments

IR Spectra were recorded on JASCO (Japan) FT-IR-5300 spectrometer at the University of Hyderabad using KBr (disk). ^{1}H and ^{13}C NMR spectra of the final dendron were recorded on a Bruker A VIII 500 MHz NMR spectrometer at IIT, Chennai, operating at 500.13 MHz for ^{1}H, 125.75 MHz for ^{13}C NMR, data were recorded in DMSO-d_6 and chemical shifts were referenced to TMS. ^{1}H and ^{13}C NMR spectra of the intermediate dendrons were recorded on a Bruker A VIII 400 MHz NMR spectrometer at Laila Impex, Vizayawada, India, operating at 400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C NMR, data were recorded in DMSO-d_6 and chemical shifts were referenced to TMS. ^{31}P NMR was recorded on Bruker ACF Supercon 200 spectrometer operating at 81 MHz at the University of Hyderabad, Hyderabad. ^{31}P NMR data were recorded in $CDCl_3$ or DMSO-d_6 and chemical shifts were referenced to 85% H_3PO_4. EI Mass spectra of intermediate compounds were recorded on JEOL GC mate at IIT, Chennai. MALDI mass spectrum of the final dendron **6** was recorded using Applied Biosystems MALDI-TOF Voyager depro spectrometer. The sample was run using Sinapic acid as the matrix with DMSO as the solvent in dried-droplet preparation method, performed at IIT-Madras, Chennai. TGA–DTA measurement was taken using TA instrument, Waterloo, USA, performed at Sri Krishnadevaraya University, Ananthapur, India. Simultaneous TGA–DTA measures both heat flow and weight changes (TGA) in a material as a function of temperature in a controlled air atmosphere were recorded. SEM operated at 20 kV, performed at the Department of Physics, S.V. University, Tirupati, India. Elemental analyzes were performed using EA 1112 Thermo Finnigan instrument, France, at the University of Hyderabad, Hyderabad, India.