Conducting Behavior of Carbosilane Dendrimers Including Palladium Ions

Chungkyun Kim*

Department of Chemistry, Dong-A University, Pusan 604-714, Korea

Bon Won Koo

Electronic Polymer Lab., Samsung Advanced Institute of Technology, P.O.Box 111, Suwon 440-600, Korea

Sang Bak Lee and Chung Kun Song

Department of Electronics Engineering, Dong-A University, Pusan 604-714, Korea

Received Jan. 25, 2002 ; Revised Apr. 9, 2002

Abstract: The conducting behavior of dendritic carbosilanes including palladium ions (Pd^{2+}) has been measured. The palladium ion containing dendrimers were prepared by the addition of palladium dichloride to double-layered dendritic carbosilanes, which consist of phenylethynyl groups (-C≡CPh) on the outmost periphery as well as phenylethenyl and propyleneoxy groups (-CH=CPh- and $(CH_2)_3O$-) in the inner shell. By measuring conductivities, palladium ion containing dendrimers revealed an increasing tendency according to the increasing number of double bonds in the inner shells of dendritic carbosilanes.

Keywords: dendrimer, carbosilane, ethynylsilane, palladium ion, conducting polymer.

Introduction

Dendrimers offer an attractive attention for material science because of their high level of applications.[1-4] Recently, a lot of researchers using the simple construction of molecular architecture have been shifted from simple preparative topology to the versatile nano-tech-materials with specific functions.[5-9] We have reported the preparative method of carbosilane dendrimers, which consist of different branching layers such as triple bonds on the outmost periphery as well as double bonds in the inner shell.[10-12] In general, one of the intriguing prospects of the dendritic architecture is the large number of end-functionality that can reveal unique chemical and physical properties.

In this report, we tried to measure the conducting behavior of the following three types of palladium ion containing carbosilane dendrimers: (1) dendrimer with 64 phenylethynyl groups on the periphery, namely G4-64PA composed of propyloxysilyl groups only in the inner shells, (2) G4E-64PA with 32 double bonds in the third generational area and 64 ethynyl groups on the periphery, and (3) G4EE-64PA consisting of 16 and 32 ethynyl groups in the second and third generational area, and 64 ethynyl groups on the periphery, respectively.[11] The three models without palladium ions didn't reveal conducting behavior in any case. Therefore, we focused our attention on palladium ions in the double-layered dendritic macromolecules with double bonds in the inner shells and triple bonds on the outmost periphery.

Experimental

The detailed synthetic methods for G4-64PA, G4E-64PA and G4EE-64PA were described in the prior report (see, ref. 11). Palladium ion containing dendrimers, G4-64PA·$(PdCl_2)_n$, G4E-64PA·$(PdCl_2)_n$ and G4EE-64PA·$(PdCl_2)_n$, were prepared by dissolving 0.1 g (7.8~6.7 μmol) of G4-64PA, G4E-64PA and G4EE-64PA in 5 mL THF followed by addition to the excess (0.2 g, 1.12 mmol) of palladium chloride. The reaction mixtures were warmed for 3 h at 50 °C, and the insoluble $PdCl_2$ precipitated to the bottom. The palladium ion adducts, G4-64PA·$(PdCl_2)_n$, G4E-64PA·$(PdCl_2)_n$ and G4EE-64PA·$(PdCl_2)_n$, were found to have good solubility in THF to yield a dark-brown clear liquid. However, the NMR spectroscopic view of the platinum ion containing dendrimers did not offer hyperfine structural information.

*e-mail : ckkim@mail.donga.ac.kr

Electric Measurements

The Si wafer was used as the substrate, while SiO_2 thickness (1000 Å) was grown by thermal oxidation. The thin films of the palladium ion containing dendrimers, G4-64PA·$(PdCl_2)_n$, G4E-64PA·$(PdCl_2)_n$ and G4EE-64PA·$(PdCl_2)_n$, were deposited by the spin-coating process under the condition of 1000 rpm for 30 seconds and they were dried in the vacuum environment of 5×10^{-5} torr at 50 °C for 30 min. The thickness of the thin films was about 1000 Å. For electric measurement, we have used the TLM structure[13] by thermal evaporation with the shadow mask was used as shown in Figure 1.

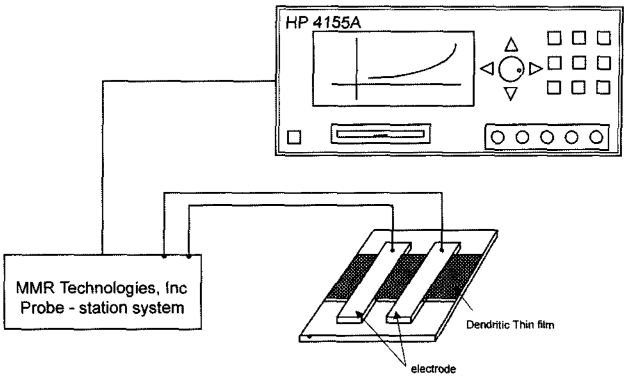


Figure 1. TML structure.

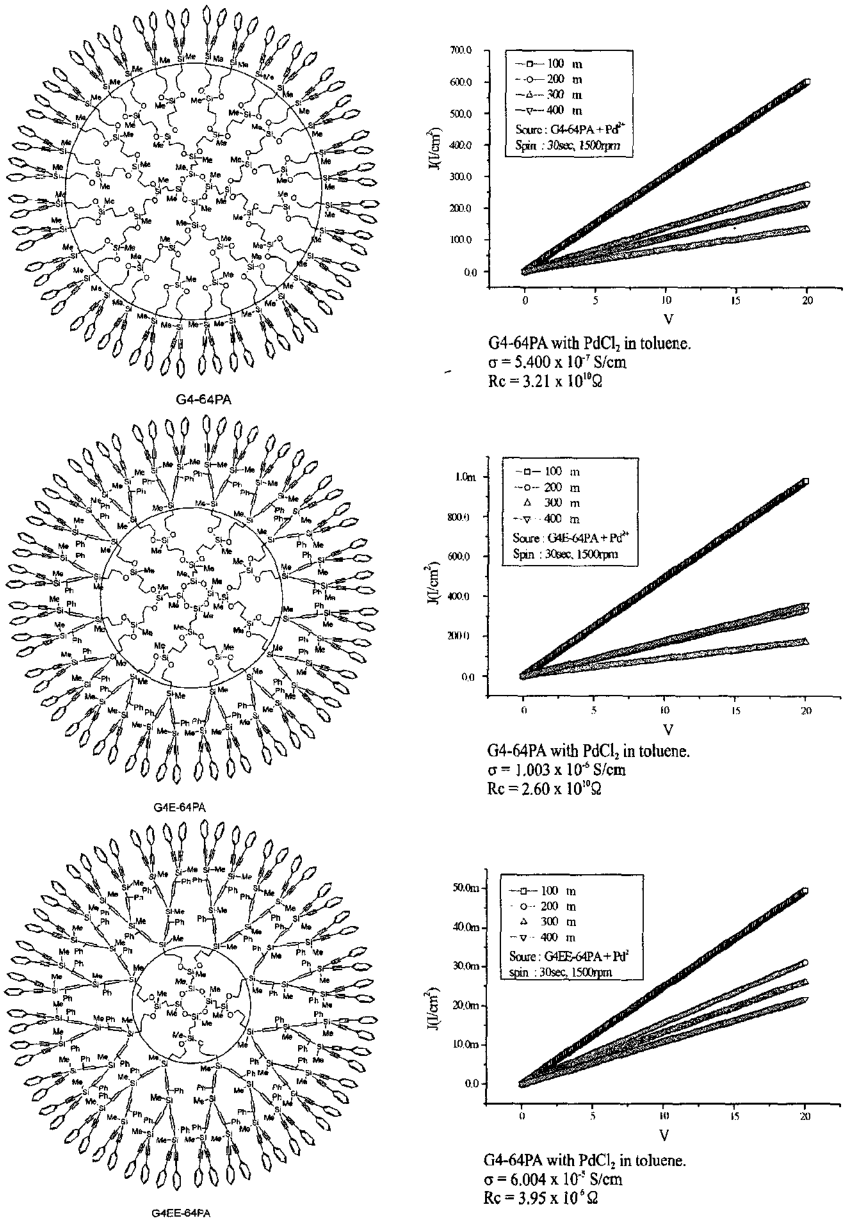
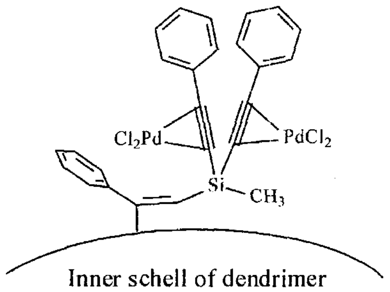


Figure 2. Planar view of urth generations and current performance of Pd^{2+} ion containing models.



Scheme I. Palladium complex on dendritic periphery.

Results and Discussion

The synthetic procedures of the double-layered dendrimers were described in the prior paper.[11] The three type of fourth generations, G4-64PA, G4E-64PA and G4EE-64PA are constructed with 64 phenylethynyl groups on the periphery and the inner shells had different numbers of double bonds. Namely, G4-64PA has no double bonds in the inner shells. G4E-64PA one ethenyl layer in the inner shell (G3) and G4EE-64PA has one propyleneoxy group containing generation in G1 and two-ethenyl group containing generations in the inner shells (G2 and G3) and 64 phenylethynyl groups on the periphery.

Our approach to depositing palladium ions inside dendrimers is simple. The predetermined amount (0.1 g, 7.8 ~ 6.7 μmol) of the dendrimers (G4-64PA, G4E-64PA and G4EE-64PA) was added in 5 mL of THF and continually added to the excess (about 0.2 g) of palladium chloride. The palladium added dendrimers, G4-64PA · $(PdCl_2)_n$, G4E-64PA · $(PdCl_2)_n$ and G4EE-64PA · $(PdCl_2)_n$, revealed a red-brown colored liquid and excess palladium ions existed as an insoluble solid in the reaction medium. The conducting behavior of the dendritic carbosilanes without palladium ions showed a very low or unmeasured current. The measurement of the conducting behavior of palladium ion containing dendrimers, G4-64PA · $(PdCl_2)_n$, G4E-64PA · $(PdCl_2)_n$ and G4EE-64PA · $(PdCl_2)_n$, revealed the value $\sigma = 5.4 \times 10^7$, 1.0×10^{-6}, and 6.0×10^{-5} S/cm, respectively (Figure 2). I-V characteristics were measured by HP4155A. The sheet resistance, contact resistance and conductance were extracted from the relations between the distance of the contacts and the sheet resistance (Figure 1). Our approach to the complexation abilities of the palladium ions between the peripheral triple bonded phenylethynyl rests and double bonds in the inner shells is very difficult to demonstrate. However we could be informed about the structural properties of the dendritic surface by metal π-complex[14] as Scheme I but we have not determined the amount of palladium ions into dendrimers.

Acknowledgment. The Ministry of Information and Communication of Korea supported this study (2001-002-02).

References

(1) G. R. Newkome, C. N. Moorefield, and F. Vögtle, *Dendritic Molecules,* VCH, Weinheim, 1996.
(2) M. Fischer and F. Vögtle, *Angew. Chem. Int. Ed.,* **38**, 884 (1999).
(3) J.-P. Majoral and A.-M. Caminade, *Chem. Rev.,* **99**, 845 (1999).
(4) S. Huang and J. M. Tour, *J. Am. Chem. Soc.,* **121**, 4908 (1999).
(5) K. Inoue, *Prog. Polym. Sci.,* **25**, 453 (2000).
(6) F. Vögtle, S. Gestermann, R. Hesse, H. Schwierz, and B. Windisch, *Prog. Polym. Sci.,* **25**, 987 (2000).
(7) A. Harada, *Acc. Chem. Res.,* **34**, 456 (2001).
(8) B. W. Koo, C. K. Song, and C. Kim, *Sensors and Actuator B,* **77**, 432 (2001).
(9) R. M.Crooks, M. Zhao, R. Sun, V. Chechik, and L. K. Yeung, *Acc. Chem. Res.,* **34**, 181 (2001).
(10) C. Kim and A. Kwon, *Synthesis,* 155 (1998).
(11) C. Kim and M. Ryu, *J. Polym. Sci. Polym. Chem. Ed.,* **38**, 764 (2000).
(12) C. Kim, E. Park, C. K. Song, and B. W. Koo, *Syn. Met.,* **123**, 493 (2001).
(13) B. W. Koo, Dissertation, Dong-A University, 2001.
(14) S. Cacchi, *J. Organomet. Chem.,* **576**, 42 (1999).