DOI: 10.1002/masy.200750338

Preparation of Buckyball-Shaped Conducting Polythiophene by the Gamma Radiation-Induced Polymerization Method

Mohammad Rezaul Karim,[1] *Chul Jae Lee,*[1] *Hee Jin Kim,*[1]
Md Tauhidul Islam Bhuiyan,[1] *Mu Sang Lee**[2]

Summary: We report on a fascinating morphology; giant spherical conducting polythiophene by the in-situ gamma radiation-induced chemical polymerization method. The resultant micron-size buckyball-shaped polymer structures were identified by high resolution transmission electron microscopy and scanning electron microscopy. Different characterizations e.g. elemental analysis, Fourier transform infrared, x-ray diffraction, and x-ray photoelectron spectroscopy were utilized to prove that the new morphological conducting polythiophene was synthesized successfully by this novel method.

Keywords: conducting polymers; morphology; polythiophene; radiation; spherical

Introduction

Electrically conducting polymers (CP) have rapidly become a subject of considerable interest among academic and industrial researchers due to their curious electronic, magnetic, and optical properties.[1–4] Polythiophene (PTh) is one of the most studied electrically conducting conjugated polymers due to its flexibility, ease of doping, and good thermal and electrical stability. PTh has been often considered as a role model for the study of charge transport in CP with a nondegenerate ground state; on the other hand, the high environmental stability of both its doped and undoped states together with its structural versatility have led to multiple developments aimed at applications in plastic photovoltaic, OLED, electrochromic or smart windows, antistatic coatings, sensors, batteries, nanoelectronic, and optical devices.[5–7] Polythiophene and its derivatives have worked very well in some of the above applications and less impressively in other devices. Creative designs and development strategies of new polythiophene have led to interesting new materials and enhanced performances in certain devices. In general, conducting polythiophenes are prepared by two main routes, i.e., chemical and electro-chemical syntheses. One of the first chemical syntheses of polythiophene was reported by two research groups Yamamoto et al. and Dudek et al. in 1980.[8,9] Both groups synthesized polythiophene by the metal-catalyzed polycondensation polymerization of 2, 5-dibromothiophene. After that, a great deal of research has been done concerning the polymerization of 2,5-dihalothiophene by varying the monomer concentrations, reaction conditions, types of metal, halogen on the monomer, and catalysts.[10–13] Sugimoto et al. has designed a very simple method for the polymerization of polythiophene and its derivatives.[14,15] This method is now well-established as one of the most widely used and straightforward methods in the preparation of PTh and its derivatives.[16–20] Wan et al. recently developed a

---

[1] Department of Chemistry, Graduate School, Kyungpook National University, Daegu 702-701, South Korea
[2] Department of Chemistry Education, Teachers College, Kyungpook National University, Daegu 702-701, South Korea
Fax: +82-539505899
E-mail: mslee@mail.knu.ac.kr

simple method of *in-situ* doping polymerization in the presence of β-naphthalene sulfonic acid as the dopant.[21] This *in-situ* doping polymerization is much easier and more popular in comparison with the other synthesis methods. More recently, gamma-irradiation has been used extensively to generate novel nano/micro particles of polymeric materials with unusual properties, since it can help prepare particles at room temperature and under the ambient pressure. It can be easily controlled and it is adaptable, nor does it induce impurities into the materials.[22–25] Here, we present a novel synthesis route and unique physical properties for a new constitutional view of spherical conducting polythiophene by the *in-situ* gamma radiation-induced oxidative polymerization method, and describe the characterizations in detail.

Experimental Part

Thiophene monomer (99%, Aldrich) was distilled under a reduced pressure and kept below 0 °C prior to use. Chloroform ($CHCl_3$), anhydrous iron (III) chloride ($FeCl_3$), and other organic solvents were bought from Aldrich as reagent grade and used without further purification. In a typical synthesis, anhydrous $FeCl_3$ (0.0129 **M**) (in a 100 ml $CHCl_3$ solution) was added to a 250 ml capacity high-density polyethylene bottle and sonicated for 10 minutes at room temperature. Thiophene monomer (0.0125 **M**) (with a 50 ml $CHCl_3$ solution) was added gradually (drop wise) to the above solution with constant stirring. The resultant solution was deaerated by bubbling with argon in order to remove the dissolved oxygen before irradiation. Then, it was sealed and radiated by a ^{60}Co γ-ray source at a rate of ca. 20 kGy for one hr, under atmospheric pressure at ambient temperatures. After irradiation, the samples were washed carefully with an excess of distilled water, methanol, hydrochloric acid (0.1 **M**), and acetone, respectively, to remove the unused initiator, and other impurities. The obtained black powder was dried under a vacuum dryer for 24 hr at room temperature.

The instruments used in this work included an elemental analysis (CE Instruments model FISON EA-1110); a field-emission scanning electron microscope (FE-SEM) (Hitachi model S-4300); a high resolution transmission electron microscope (HR-TEM) (Philips model CM 200) with an Acc. Voltage of 200kv; a Fourier transform infrared (FT-IR) (Bruker IFS 120HR); an x-ray diffraction (XRD) (Philips model X'Pert APD) with a Cu Kα source; a thermal gravimetric analysis (TGA) (Dupont model 9900/2100) in a nitrogen atmosphere, at a heating rate of 10 °C/min in the temperature range between 0–800 °C; and an x-ray photoelectron spectroscopy (XPS) (VG Clam2 system). The room-temperature conductivity of the pressed pellets was measured by the standard four-point probe method, using a Jandel engineering instrument, model CMT-SR1060N.

Results and Discussion

Typical morphology of spherical PTh was investigated using a field-emission scanning electron microscopy and a high-resolution transmission electron microscopy. As shown in Figure 1, the FE-SEM images show a uniform view of individual (Figure 1a) and group (Figure 1b) spherical conducting polythiophene, with particles in micrometer scale (e.g. 0.5–10 μm), as well as larger giant particles. A similar morphological structure of sphere-shaped virgin polythiophene was also imaged by HR-TEM, as shown in Figure 1c. From electron microscope images, it identified clearly that the conducting polythiophene formed new morphology as like buckyball structure and some of their inside were hollowed. These structures were found from the parent solutions with typical concentrations of 0.0125 **M** of thiophene and 0.0129 **M** of anhydrous ferric chloride, in chloroform solutions as described in detail in the experimental section. To

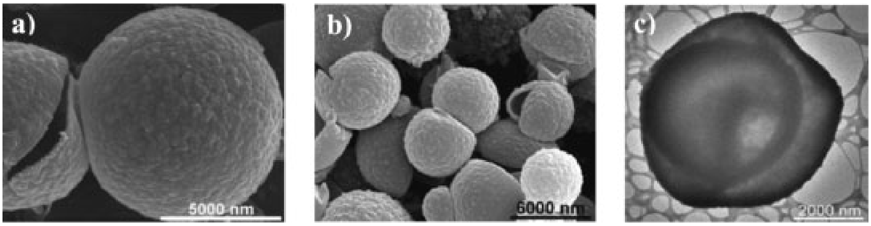

Figure 1.
FE-SEM images of (a) single, (b) groups, and (c) HR-TEM image of giant spherical conducting polythiophene synthesized by the *in-situ* gamma radiation-induced chemical polymerization method.

observe the effects of the monomer and oxidant concentrations, we used different amounts of monomer and oxidant as shown in Figure 2. We found the best yield of spherical polythiophene components with 0.0125 **M** of thiophene and 0.0129 **M** of anhydrous ferric chloride in the chloroform solution (Figure 2a). In the following discussion, we will give only the explanation for this sample. Moreover, we used two gamma radiation doses (5 and 20 kGy for one hr) for all samples, but the same results were observed in both cases. The chemical composition of the resultant sphere-shaped conducting PTh was also calculated by an elemental analysis method. The data show that the composition is approximately: C 54.03, H 2.81, N 0.11, and S 26.77 for this pristine spherical PTh.

Proof of the polythiophene component was provided by FT-IR and XRD data, as shown in Figure 3. In FT-IR spectrum

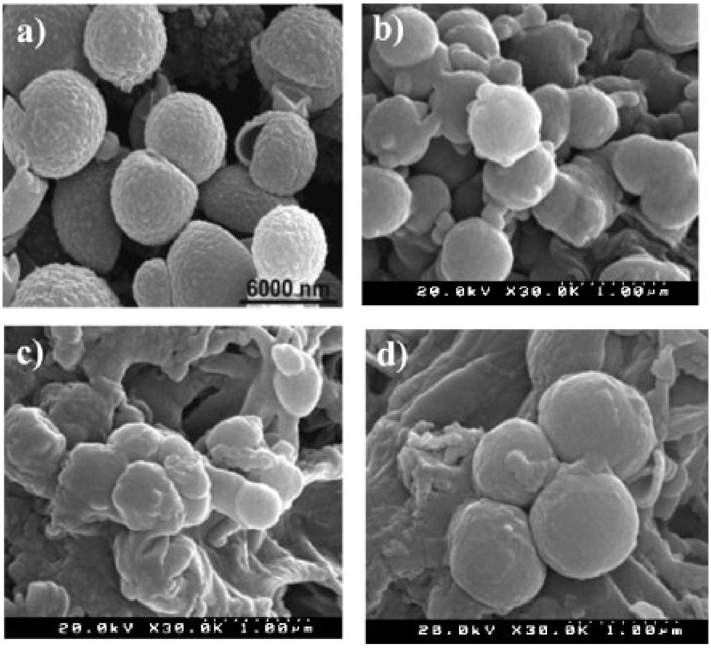

Figure 2.
FE-SEM images showing the effect of monomer (thiophene) and oxidant (anhyd. $FeCl_3$) concentrations of (a) 0.0125 **M**: 0.0129 **M** (scale bar: 6 μm), (b) 0.0125 **M**: 0.0065 **M** (scale bar: 1 μm), (c) 0.0063 **M**: 0.0065 **M** (scale bar: 1 μm), and (d) 0.0063 **M**: 0.0129 **M** (scale bar: 1 μm), respectively for the spherical conducting polythiophene synthesized by the *in-situ* gamma radiation-induced chemical polymerization method.

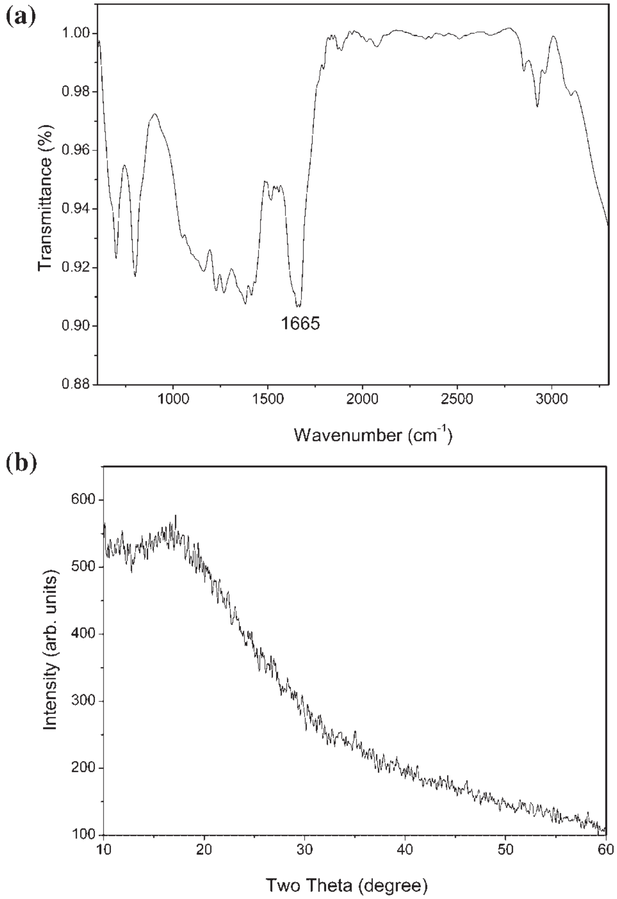

Figure 3.
(a) FT-IR and (b) XRD analysis data of spherical conducting polythiophene synthesized by the *in-situ* gamma radiation-induced chemical polymerization method.

(Figure 3a), there are several low intensity peaks present in the range between 2800–3100 cm^{-1}, which can be attributed to aromatic C–H stretching vibrations.[26,27] The absorption in this region is obscured by the bipolaron absorption of the doped PTh. The range of 600–1500 cm^{-1} is the fingerprint region of PTh. The peak at approximately 798 cm^{-1} is usually ascribed to the aromatic C–H out-of-plane deformation mode as reported by other groups,[28] while other peaks in this region can be attributed to the ring stretching modes. The C–S bending mode was identified at approximately 702 cm^{-1}, which indicates the presence of a thiophene monomer.[29] The 1665 cm^{-1} peak could be due to conjugated carbonyl species within the polymer backbone as suggested by other groups.[30–33] It assumes that most of the excess oxygen is present as a dopant, probably in the form of O^{2-}. Will and McKee[34] showed that undoped polyacetylene absorbs in excess of 40% by weight of oxygen at room temperature. Beck et al. found that the excess oxygen was the result of over oxidation of polymer with water as a nucleophile.[35] Yang and Chien[36] proposed several reactions relating autooxidation of a conjugated polymer represented by polyacetylene where the oxidative degradation primarily proceeds with peroxy radicals formed in the polymer backbones. In Figure 3b, the XRD pattern exhibits a broad amorphous diffraction peak at approximately $2\theta = 14 \sim 19^\circ$ ranges. This broad peak centered at around 17° corresponding to intermolecular π-π stacking emerges for polythiophene.[37]

To further clarify the chemical situation of the elements, we measured the XPS of the samples. The S-2p core-level spectrum of the PTh (Figure 4a) can be deconvoluted into at least two spin-orbit-split doublet ($S\text{-}2p_{3/2}$ and $S\text{-}2p_{1/2}$) peaks at approximately 164.2 and 164.9 eV, which are attributed to the neutral sulphur atoms, respectively.[38] This indicates that the chemical environment of the S element, in pure PTh is almost identical.

Thermal stability testing was conducted using the thermal gravimetric analysis. Figure 4b shows the weight loss of polythiophene powders upon heating in a nitrogen atmosphere. PTh was initially rather stable up to the temperature of 150 °C. From 150 °C on a continuous degradation was found up to the highest temperature. The total mass loss in the region between 0 °C and 800 °C for spherical conducting polythiophene was estimated to be about 34.5% by this novel synthesis.

In general, electrical conductivity may be taken as a function of the conjugation length of the polymer and of the amount of active dopant present in the polymer, as the number of charge carriers depends upon

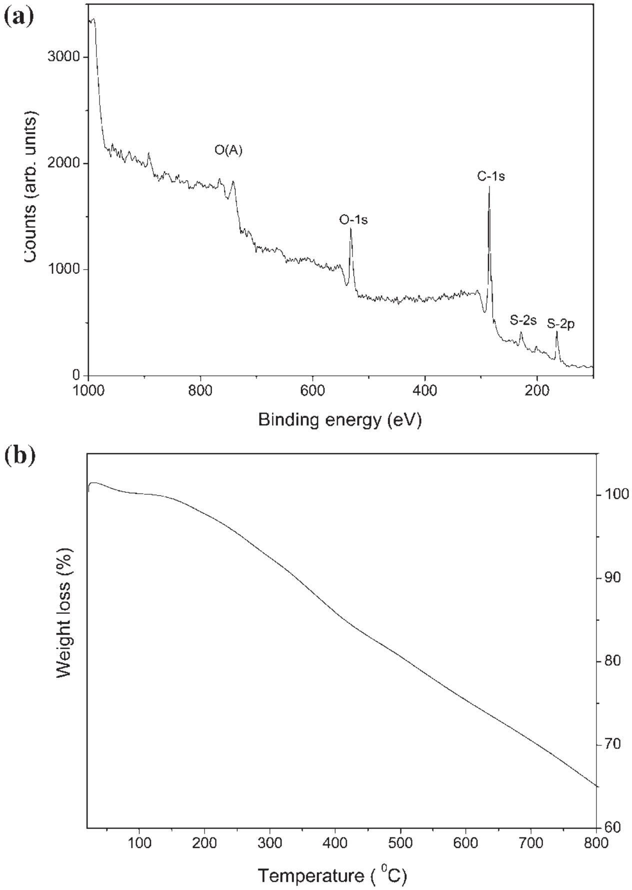

Figure 4.
(a) XPS and (b) TGA data of spherical conducting polythiophene synthesized by the *in-situ* gamma radiation-induced chemical polymerization method.

the extent of the dopant concentration, providing that other factors remain unchanged. The conductivity has been calculated for this sphere-shaped conducting polythiophene by the *in-situ* gamma radiation-induced oxidative polymerization method about 2.4×10^{-4} S/cm. For the conductivity reported here, the result was an average of five measurements.

The mechanism of giant spherical conducting polythiophene formation by the *in-situ* gamma radiolysis chemical polymerization method is still somewhat complicated. However, it is important to discuss some relevant issues which were observed in this work. In our approach, gamma radiation induced the thiophene monomers to be polymerized in very large quantities; buckyball-shaped structures were solidified at room temperature under the ambient conditions. Ionizing radiation affected only polymer morphology, but it did not have a affect in the polymerization reaction. In addition, we didn't observe any spherical morphology for conducting polythiophene by similar procedures, such as *in-situ* oxidative polymerization method without gamma irradiation.[39] Thus, it can be assume that buckyball-shaped conducting polythiophene self-assembles by the in-situ gamma radiolysis chemical polymerization method. The detailed formation mechanism of the spherical conducting polythiophene needs to be investigated further. Experiments are in progress and we hope to report on the results in near future.

Conclusions

We have demonstrated a new morphology, micrometer particle sizes of buckyball-shaped giant spherical conducting polythiophene synthesized by the *in-situ* gamma radiolysis chemical oxidative polymerization method. Different structural characterizations including electron microscope images and spectroscopy analysis data clearly indicated that the spherical conducting polythiophene were synthesized successfully by this novel route. Electrical and thermal analysis data also showed the moderately good values for these pristine sphere-shaped conducting polythiophene. It is hypothesized that, because of the simplicity and robustness of this procedure, these giant morphology of virgin spherical polythiophene could initiate new research among academic and industrial researchers.

Acknowledgements: The authors gratefully acknowledge the financial support of the Korea Research Foundation (Grant No. KRF-2006-005-J02401).

[1] C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A. G. MacDiarmid, *Phys. Rev. Lett.* **1977**, *39*, 1098.
[2] S. P. Economopoulos, G. K. Govaris, C. L. Chochos, N. P. Tzanetos, A. K. Andreopoulou, J. K. Kallitsis, P. Yianoulis, V. G. Gregoriou, *Macromol. Symp.* **2004**, *205*, 19.
[3] M. R. Karim, C. J. Lee, Y. T. Park, M. S. Lee, *Synth. Met.* **2005**, *151*, 131.
[4] *Handbook of Conducting Polymers*, T. A Skotheim, R. L Elsenbaumer, J. R. Reynolds, Eds., 2nd ed., Marcel Dekker, New York **1998**.
[5] J. Roncoli, *Chem. Rev.* **1992**, *92*, 711.
[6] R. D. McCullough, *Adv. Mater.* **1998**, *10*, 93.
[7] E. Jaehne, D. Ferse, H. J. P. Adler, K. Ramya, I. K. Varma, M. Wolter, N. Hebestreit, W. Plieth, *Macromol. Symp.* **2001**, *164*, 133.
[8] T. Yamamoto, K. Sanechika, A. Yamamoto, *J. Polym. Sci. Polym. Lett. Ed.* **1980**, *18*, 9.
[9] J. W. P. Lin, L. P. Dudek, *J. Polym. Sci. Polym. Chem. Ed.* **1980**, *18*, 2869.
[10] T. Yamamoto, K. Sanechika, A. Yamamoto, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1497.
[11] C. Z. Hotz, P. Kovacic, I. A. Khoury, *J. Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 2617.
[12] M. Kobayashi, J. Chen, T. C. Chung, F. Moraes, A. J. Heeger, F. Wudl, *Synth. Met.* **1984**, *9*, 77.
[13] T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z. H. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, K. Kubota, *Macromolecules* **1992**, *25*, 1214.
[14] K. Yoshino, S. Hayashi, R. Sugimoto, *Jpn. J. Appl. Phys.* **1984**, *23*, L899.
[15] R. Sugimoto, S. Takeda, H. B. Gu, K. Yoshino, *Chem. Express* **1986**, *1*, 635.
[16] K. Yoshino, S. Nakajima, R. Sugimoto, *Jpn. J. Appl. Phys.* **1987**, *26*, L1038.
[17] S. Hotta, M. Soga, N. Sonoda, *Synth. Met.* **1988**, *26*, 267.
[18] M. Leclerc, F. M. Diaz, G. Wegner, *Makromol. Chem.* **1989**, *190*, 3105.
[19] M. S. A. Abdou, X. Lu, W. Xie, F. Orfino, M. J. Deen, S. Holdcroft, *Chem. Mater.* **1995**, *7*, 631.

[20] F. Chen, P. G. Mehta, L. Takiff, R. D. McCullough, *J. Mater. Chem.* **1996**, *6*, 1763.
[21] Y. Shen, M. Wan, *J. Polym. Sci. Polym. Chem.* **1997**, *35*, 3689.
[22] Y. Xie, Z. Qiao, M. Chen, X. Liu, Y. Qian, *Adv. Mater.* **1999**, *11*, 321.
[23] S. Milojković, D. Kostoski, J. Čomor, J. M. Nedeljković, *Polymer* **1997**, *38*, 2853.
[24] T. Seguchi, T. Yagi, S. Ishikawa, Y. Sano, *Rad. Phys. Chem.* **2002**, *63*, 35.
[25] X. Zhang, M. Wang, T. Wu, S. Jiang, Z. Wang, *J. Am. Chem. Soc.* **2004**, *126*, 6572.
[26] Y. D. Wang, M. F. Rubner, *Synth. Met.* **1990**, *39*, 153.
[27] J. X. Wang, *Electrochim. Acta* **1996**, *41*, 2563.
[28] N. Toshima, S. Hara, *Prog. Polym. Sci.* **1995**, *20*, 155.
[29] Y. A. Udum, K. Pekmez, A. Yildiz, *Eur. Polym. J.* **2005**, *41*, 1136.
[30] P. Pfluger, M. Krounbi, G. B. Street, G. Weiger, *J. Chem. Phys.* **1983**, *78*, 3212.
[31] J. C. Scott, P. Pfluger, M. Krounbi, G. B. Street, *Phys. Rev. B* **1983**, *28*, 2140.
[32] O. Nishikawa, H. Kato, *J. Chem. Phys.* **1986**, *85*, 6758.
[33] G. I. Mathys, V. T. Troung, *Synth. Met.* **1997**, *89*, 103.
[34] F. G. Will, D. W. McKee, *J. Polym. Sci.* **1983**, *21*, 3479.
[35] F. Beck, P. Braun, M. Oberst, *Ber Bunsenges Phys. Chem.* **1987**, *91*, 967.
[36] X. Z. Yang, J. C. W. Chien, *J. Polym. Sci. Polym. Phys. Ed.* **1985**, *23*, 859.
[37] Y. Li, G. Vamvounis, S. Holdcroft, *Macromolecules* **2002**, *35*, 6900.
[38] E. T. Kang, K. G. Neoh, K. L. Tan, *Phys. Rev. B* **1991**, *44*, 10461.
[39] M. R. Karim, C. J. Lee, M. S. Lee, *J. Polym. Sci. Polym. Chem.* **2006**, *44*, 5283.