

Copyright © 2013 American Scientific Publishers All rights reserved Printed in the United States of America Journal of Nanoscience and Nanotechnology Vol. 13, 6130–6135, 2013

Synthesis and Preparation of Fluorinated Polycarbonates Enhancing the Light Absorption of Fluorescent Nanoparticles

Teahoon Park, Syed Nawazish Ali, Jungmok You, Byeonggwan Kim, and Eunkyoung Kim*

Active Polymer Center for Pattern Integration, Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, South Korea

A new synthetic method for fluorinated polycarbonates without the use of any toxic phosgene gas is presented. The synthesis consists of a monomer synthesis followed by polymerization. The fluorinated polycarbonate (FPC) was confirmed by Fourier transform infrared spectroscopy (FT-IR) and NMR spectroscopy. The refractive index of the polymer was 1.466 determined by an Abbe refractometer. The contact angle measurement of the FPC films showed the hydrophobicity with water contact angle about 112.6°. These films of varying thicknesses had over 98% transmittance. Taking advantage of the hydrophobicity and high transmittance of the FPCs, nanoparticles of FPCs were prepared directly in an aqueous solution with a reprecipitation method. Combining FPC solution with a solution containing fluorescent polymer (DTMSPV), nanoparticles with a core–shell structure were obtained easily with the reprecipitation method. The fluorescence intensity of the DTMSPV in the core–shell nanoparticles were much enhanced up to 34.1% compared to the molecularly dispersed DTMSPV solution.

Keywords: Fluorinated Polycarbonate, Enhanced Fluorescence, Core–Shell Nanoparticle, Reprecipitation Method.

1. INTRODUCTION

Fluorinated polymers have attracted much attention due to their use in a vast variety of applications, such as optical communication systems, optical filters, and antireflection films used in displays and coatings, but mainly because of their low optical loss and high resistance.^{1–5} It is well known that increasing the fluorine content of a polymer enhances their unique characteristics.^{6–9} Perfluoropolymers, which contain mainly C—F bonds, have excellent chemical and weather resistance. The small dipole moment of these compounds also contributes to their oil and water-repellency as well as their low surface tension, low friction coefficient and reduced adhesion to surfaces.¹⁰ Therefore, fluorinated polycarbonates could be an ideal media or encapsulant for active organic molecules.

However, most of the fluorinated polymers have severe shortcomings including poor adhesion to substrates and low transparency that arises from the high surface energy and crystalline properties of the fluorine compounds, which have limited their use in industrial applications.¹¹ Recently, novel fluorinated polymers were synthesized by combining a fluorinated group and other functional groups such as urethane¹² to overcome some of these shortcomings as well as to achieve some of the desired functionalities.

In our previous studies, we reported that photopolymerizable perfluorinated methacrylates have a polar functional carbonate (-O-C(=O)-O-), which showed improved optical and adhesion properties for optical waveguide materials.^{2, 5, 13-15} The adhesion of perfluorinated methacrylate onto such substrates as glasses and silicon wafers was enhanced by the introduction of a carbonate, a polar functional group.

Herein, we report the synthesis of a new fluorinated polycarbonate (FPC) by direct polymerization without phosgene gas to fabricate a FPC with high transparency, hydrophobicity and good film properties. In addition, we report in this study the formation of FPC nanoparticles

^{*}Author to whom correspondence should be addressed.

^{1533-4880/2013/13/6130/006}

and core–shell FPC nanoparticles containing fluorescent polymers which can be used for many applications.^{16, 17}

2. EXPERIMENTAL DETAILS

2.1. Materials

Fluorinated diol, 1H,1H,6H,6H-perfluoro-1,6-hexanediol, and fluorinated tetra ethylene glycol were purchased from Exfluor Research Corporation, USA. Pyridine, 18-crown-6, 1,1'-carbonyl diimidazole, 4-nitrophenyl chloroformate, and 1,4-benzenedimethanol were purchased from Aldrich chemicals. Other solvents such as tetrahydrofuran (THF) and dichloromethane (MC) for the synthesis were prepared from Aldrich chemicals and used after distillation.

2.2. Synthesis of FPC Monomers

A solution of 4-nitrophenyl chloroformate (6.44 g, 32.0 mmol) in anhydrous dichloromethane (40 mL) was added dropwise with a 100 mL dropping funnel into a solution of 1H,1H,6H,6H-perfluoro-1,6-hexanediol (4.22 g, 16.0 mmol) in anhydrous pyridine (2.53 g, 32.0 mmol) and anhydrous dichloromethane (30 mL) in a 250 mL round-bottom flask. The mixture was allowed to stir gently at room temperature for 18 hours. Then, anhydrous dichloromethane (40 mL) was added and the reaction mixture was stirred for another 6 hours. The reaction mixture was then quenched by adding deionized water (30 mL). The solution was then washed with deionized water (25 mL \times 2), followed by a 5.0% solution of acetic acid (50 mL \times 3) and then finally washed again with deionized water (50 mL \times 2). The solution was dried with anhydrous $MgSO_4$ and the solids were filtered off. The solvent and volatile impurities were removed with a rotary evaporator. The resulting product was recrystallized from methanol (30 mL) to afford a white crystalline solid product with good yield (9.1 g, 95.4%).

¹H NMR (300 MHz, ppm, CDCl₃); δ 8.31 (*d*, 4H, ArCH–'C–NO₂), δ 7.40 (*d*, 4H, ArCH–'C–O), δ 4.78 (*t*, 4H, CF₂CH₂O); ¹⁹F NMR (282.78 MHz, ppm, CDCl₃); δ -123.5, δ -119.4; ¹³C NMR (75 MHz, ppm, CDCl₃); δ 155.0 (C=O), δ 151.7 (*C–O), δ 145.9 ('C–NO₂), δ 125.5 (ArCH–'C–NO₂), δ 121.6 (ArCH–*C–O), δ 114.3 (CF₂, weak signal), δ 111.5 (CF₂, weak signal), δ 63.7 (CH₂–O).

2.3. Synthesis of FPC

In a 250 mL round-bottom flask, 1,4-benzenedimethanol (0.7 g, 5.06 mmol), bis-nitrophenylcarbonate of fluorinated diol (3 g, 5.06 mmol), 18-crown-6 (0.31 g, 1.18 mmol) and anhydrous potassium carbonate (3.5 g) were mixed. This reaction flask was flushed with argon and was subjected to five vacuum-argon cycles, and then anhydrous CH_2Cl_2 (40 mL) was added. The reaction mixture was

J. Nanosci. Nanotechnol. 13, 6130-6135, 2013

stirred vigorously and refluxed at 50 °C for 65 hours. After cooling the reaction mixture to room temperature, fresh CH_2Cl_2 (30 mL) was added to the reaction mixture. The mixture was then centrifuged, and the solids were filtered off and then the mixture washed with a saturated solution of sodium bicarbonate (40 mL). The organic phase was then washed with deionized water (30 mL × 2), a saturated solution of sodium bicarbonate (30 mL × 3) and then finally washed again with deionized water (30 mL × 3). The solution was then dried with anhydrous MgSO₄. After filtrating off the solids, the solvent was removed *in vacuo* to afford oily products, which were reprecipitated from a mixture of CH_2Cl_2 (~3 mL) and methanol (250 mL) to yield 1.75 g of product (yield = 86%) as a white solid.

¹H NMR (300 MHz, ppm, CDCl₃); δ 4.62 (4H, CH₂CF₂), δ 5.20 (*s*, 4H, CH₂Ar), δ 7.37 (*s*, 4H, CH– Ar); ¹⁹F NMR (282.78 MHz, ppm, CDCl₃): δ-125.6, δ-120.0; ¹³C NMR (75 MHz, ppm, CDCl₃); δ 155.0 (C=O), δ 136.0 (*C–CH₂–O), δ 128.7 (ArCH-*C–CH₂– O), δ 114.3 (CF₂, weak signal), δ 112.1 (CF₂, weak signal), δ 70.27 (*C–CH₂–O), δ 62.9 (CH₂–O).

2.4. Preparation of FPC Nanoparticles and FPC Coated Fluorescent Polymer Nanoparticles

Using a 1 wt% solution of FPC in a mixture of chloroform and dichloromethane (9:1), polymer films having different thickness from 100 to 500 nm were prepared by spin coating at $1000 \sim 3000$ rpm for 30 s. The films were then annealed at 70 °C for 30 min. These polymer films were used for spectroscopic measurements to confirm the transmittance and contact angle measurements.

FPC nanoparticles were prepared following the reprecipitation method.¹⁸ The concentration of FPC in THF was varied from 0.25 mg/mL to 1 mg/mL to obtain the optimum size distribution. The FPC solution (100 μ L) was then injected into a 5 mL fluorescent polymer aqueous solution under sonication. The water-soluble triazinebridged copolymer, poly[(diphenylamino-s-triazine)-co-(2-methoxy-5-propyloxysulfonate-1,4-phenylenevinylene)] (DTMSPV) was used as a fluorescent polymer which had been studied in our previous report.¹⁹ The solution was then heated in a microwave oven to remove the organic solvent and promote the formation of DTMSPV/FPC nanoparticles. All solution samples were then cooled to room temperature before characterization.

2.5. Characterization

UV-visible absorption and transmittance spectra were measured with a UV-vis-NIR spectrometer (PerkinElmer, Lambda 750, USA). Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a TENSOR 37 (Bruker). The fluorescence spectra were obtained with a luminescence spectrometer (Perkin Elmer, Model LS55) under excitation at 370 nm. ¹H NMR analysis was conducted in a BRUKER DPX 300 MHz spectrometer. Chloroform-d (CDCl₃) was used as the solvent, and tetramethylsilane (TMS) was used as the internal standard. The average molecular weight of the polymer was characterized by gel permeation chromatography (GPC) (model: Waters R-401 ALC/GPC) with THF as the eluent and polystyrene was used as the standard for calibration. The thickness of the polymer films was determined using an Alpha-step profilometer (Tencor Instruments, Alphastep IO) with an accuracy of 1 nm. The surface wettability was investigated by distilled water (DI) drop contact angle measurements using a contact angle meter-CAM 101 model (KSV Instruments Ltd., Finland). More than five readings were obtained for each sample; the average value is reported. Weight loss measurements under controlled heating were carried out with a thermogravimetric analysis instrument TGA 2050 (TA instrument). It was used to determine the thermal decomposition temperature of the fluorinated polymers. Scanning electron microscopy (SEM) images were obtained with a field emission scanning electron microscope (FE-SEM) system JEOL-6701F. Transmission electron microscopy (TEM) JEM-2010 was used to make sure the formation of core-shell nanoparticles. The zeta potential of the nanoparticles was investigated with the ZEN 2001 (Malvern Instruments).

3. RESULTS AND DISCUSSION 99.174.178 On: F

3.1. Synthesis and Characterization of FPC

The fluorinated bis-nitrophenylcarbonate (FNPC) monomers were synthesized as described in Figure 1. The goal of the polymerization was to incorporate a functional group such as a carbonate as part of the fluorinated polymer. The FPC was synthesized by reacting a diol with FNPCs in a dry CH₂Cl₂ solution in the presence of anhydrous carbonate and 18-Crown-6 (Fig. 1). resulting in an 86% yield as a white solid.²⁰ The weight average molecular weight (M_w) of FPC was 10,570 with a polydispersity index (PDI) of 1.32. The fluorine content in the polymer was 34%. Figure 2(a) shows the FT-IR spectra of the FNPC (monomer) and FPC. The polymerization of the FNPC monomers was confirmed by the disappearance of the NO₂ peaks at 1350 and 1540 cm⁻¹ in the FT-IR



Fig. 2. (a) FT-IR spectra of (I) the monomer and (II) polymer (FPC), and (b) 1 H NMR spectrum of FPC.

spectra. The ¹H NMR spectrum shown in Figure 2(b) also confirmed the polymerization. ^{of Medicine}

The thermogravimetric analysis (TGA) curve of FPC is shown in Figure 3. The mass loss of FPC began at 341 °C. This temperature is over 50 °C higher than the degradation starting temperature of the fluorine-free polymers which are similar in structure to FPC.^{20–22} The thermal degradation temperature of FPC was similar to that of bisphenol A polycarbonate. This similarity could be attributed to the number of benzene ring structures in the repeating units of the two polymers.

The refractive index of FPC was lower compared to normal polycarbonates containing C—H bonds, due to the presence of fluorine in FPC.^{23, 24} Thus the refractive index of FPC was 1.4665 with a monitoring wavelength of 589 nm, while that of bisphenol A polycarbonate was $1.55.^{25}$

The contact angles of the FPC films were $112.6 \pm 0.6^{\circ}$, using water to determine the relative wettability of the



Fig. 1. (a) Synthesis of the bis-nitrophenylcarbonate monomer used for the fluorinated polycarbonate synthesis and (b) polymerization to synthesize fluorinated polycarbonates.

J. Nanosci. Nanotechnol. 13, 6130-6135, 2013



Fig. 3. Thermogravimetric analysis of FPC conducted at a heating rate of 10 $^{\circ}$ C per minute in a nitrogen atmosphere.

FPC film surfaces. There was no significant difference as a function of film thickness from 100 to 500 nm. The surface of the FPCs was found to have become more hydrophobic due to the fluorine substitution. This can be attributed to the intrinsic low surface energy of fluoropolymers as observed for polytetrafluoroethylene (PTFE) and perfluoroalkoxy (PFA).²⁶

Figure 4 shows the transmittance depending on the film thickness. Usually fluorinated polymers have high crystallinity and thus show poor transmittance.¹¹ However, the FPC film had a high transparency of 98% in the range of from 400 to 800 nm and such high transmittance was maintained in films of up to 500 nm in thickness. Such a high transparency ensures the application of FPCs as a low refractive index film and protective coating layer for functional materials such as fluorescent polymers.

3.2. Preparation of FPC Nanoparticles and FPC Coated Fluorescent Polymer Nanoparticles

FPC nanoparticles (FPC NPs) were readily prepared by following the reprecipitation method.¹⁶ Briefly, the FPC solution in THF was injected into insoluble solvent (water) under sonication to afford nanoparticles upon evaporation of the THF at 65 °C. These nanoparticles were confirmed by FE-SEM images shown in Figure 5(a).

FPC coated fluorescent polymer nanoparticles were similarly prepared using FPC solution (100 μ L), which was injected into a 5 mL aqueous solution of fluorescent triazine-bridged copolymer (DTMSPV) under sonication. The solution was then heated in a microwave oven to remove the organic solvent and promote the formation of DTMSPV/FPC nanoparticles.

In a 5 mL DTMSPV aqueous solution $(1.65 \times 10^{-5} \text{ M})$, 100 μ L of FPC solution dissolved in THF was directly injected in order to fabricate the fluorescent nanoparticles coated with FPC. The size of the nanoparticles became larger than the size of the DTMSPV nanostructures. As the concentration of the FPC solution increased from 0.25 mg/mL to 1 mg/mL in THF solution, the size of the core–shell nanoparticles increased as well (Figs. 5(c) and (d)).





Fig. 4. Transmittance of FPC films with different thicknesses. The average value of the transmittance was calculated for wavelengths between 400 nm to 800 nm.

The structures of the FPC coated fluorescent nanoparticles in the inset of Figures 5(c) and (d) show a core-shell structure. The nanoparticle structure was further examined by TEM (inset, Fig. 5(d)). A core-shell structure was clearly shown due to the contrast difference between FPC and DTMSPV, indicating the bright shell of FPC with wall thickness of ~ 20 nm. The presence of FPC at the shell was further confirmed by the zeta potential data. The zeta potential of the DTMSPV aqueous solution and FPC nanoparticle solution were -46.1 mV and -37.0 mV, respectively. Interestingly the zeta potential of the FPC coated DTMSPV nanoparticle solution was the same as that of the FPC nanoparticle solution shown in Figure 6(a), indicating that the FPC layer formed on the outer surface of the DTMSPV. Other previous works have also demonstrated the formation of encapsulated nanoparticles by the reprecipitation method.27,28



Fig. 5. FE-SEM images of (a) FPC NPs, (b) DTMSPV, and core–shell nanoparticles fabricated by the injection of different concentrations of FPC solutions of (c) 0.25 and (d) 1 mg/mL into the DTMSPV aqueous solution. All images were obtained at the same magnification of 10,000×. The scale bar represents 1 μ m. ((c), Inset) Enlarged FE-SEM image of the DTMSPV encapsulated by FPC. ((d), Inset) TEM image of encapsulated nanoparticles.



Fig. 6. (a) The zeta potential of DTMSPV, FPC NP solution and coreshell NPs. (b) UV-Visible spectra and (c) fluorescent spectra of FPC nanoparticle solution (dashed line), DTMSPV solution (solid line), and core-shell NPs solutions prepared with different concentrations of FPC solution (red: 1 mg/mL, blue: 0.5 mg/mL, green: 0.25 mg/mL). (b), (c) inset: Photographic images of the solutions are depicted. Starting on the left with DTMSPV no FPC addition, followed by three solutions of varying additions of FPC: 0.25, 0.5, 1 mg/mL, respectively, and FPC NPs solution.

Importantly, the solution of the DTMSPV/FPC coreshell nanoparticles showed enhanced absorbance and fluorescence compared to the original DTMSPV solution at the same concentration (Figs. 6(b) and (c)). The FPC NP aqueous solution, on the other hand, was transparent and did not show any fluorescence. The fluorescence quantum yield of the DTMSPV/FPC solution was 31%, which was similar to that of the DTMSPV solution without FPC coating. Thus, the enhanced fluorescence must originate from the increased absorption as indicated in the UV spectra. The increased absorption could be attributed to the FPC layer of the DTMSPV/FPC core-shell nanoparticles which serves as a light collector. Since the refractive index of the FPC is larger than the media, the input light can be reflected by the neighboring particles that can be reabsorbed at the DTMSPV/FPC nanoparticles like a scattering and pattern effect applied to the light emitting diodes (LED) and solar cells.^{29,30,31} Since the FPC is highly transparent, the light loss by the FPC layer is small; thus, the increase in absorption should be more visible to enhance the fluorescence. Further study on this interesting light harvesting by the transparent FPC coating is in progress to optimize the structure and stability of the nanoparticles containing functional molecules.

4. CONCLUSIONS

We studied FPCs and found a new synthesis method that does not require the use of harmful gas. This synthesis consists of fluorinated monomer synthesis followed by polymerization. The FPCs were confirmed by FT-IR and NMR and the molecular weights of the polymers were obtained by GPC. Polymer films of various thicknesses could be made with the FPCs. These films of varying thicknesses had over 98% transmittance. The thermal properties of the FPCs were also analyzed by TGA, revealing high thermal stability. A core-shell nanoparticle solution was obtained in the fluorescent polymer (DTMSPV) solution with the reprecipitation method. The nanostructures of DTMSPV were encapsulated by the FPCs due to the hydrophobicity of the FPCs. The formation of core-shell nanoparticles was confirmed by FE-SEM, TEM and zeta potential measurements. The input light can be reflected from the FPC shell and reabsorbed at the neighboring core-shell nanoparticles with no significant energy loss due to the high transmittance of the FPC layer. Therefore, the light absorption of the DTMSPV inside the transparent FPC shell was enhanced and emitted high fluorescence.

Acknowledgments: We acknowledge the financial support of the National Research Foundation (NRF) grant funded by the Korean government (MEST) through the Active Polymer Center for Pattern Integration (APCPI) (R11-2007-050-00000-0), the Pioneer Research Center Program (2011-0001672), and the Converging Research Center Program (2011K000631).

References and Notes

- 1. W. E. Moerner and S. M. Silence, Chem. Rev. 94, 127 (1994).
- 2. E. Kim and S. Y. Cho, Mol. Cryst. Liq. Cryst. 377, 385 (2002).
- 3. P. Gunter and J. P. Huignard, Photorefractive Materials and Their Applications, Springer, City (1988), Vol. 1.
- H. Ma, A. K. Y. Jen, and L. R. Dalton, *Adv. Mater.* 14, 1339 (2002).
- E. Kim, S. Y. Cho, D.-M. Yeu, and S.-Y. Shin, *Chem. Mater.* 17, 962 (2005).
- T. Davidson, A. C. Griffin, L. M. Wilson, and A. H. Windle, *Macro-molecules* 28, 354 (1995).

J. Nanosci. Nanotechnol. 13, 6130-6135, 2013

- J. W. Kang, J. P. Kim, W. Y. Lee, J. S. Kim, J. S. Lee, and J. J. Kim, J. Lightwave Technol. 19, 872 (2001).
- 8. M. Yano, T. Taketsuga, K. Hori, H. Okamoto, and S. Takenaka, *Chem-Eur. J.* 10, 3991 (2004).
- 9. T. Doi, Y. Sakurai, A. Tamatani, S. Takenaka, S. Kusabayashi, Y. Nishihata, and H. Terauchi, *J. Mater. Chem.* 1, 169 (1991).
- J. Liang, E. Toussaere, R. Hierle, R. Levenson, J. Zyss, A. V. Ochs, A. Rousseau, and B. Boutevin, *Opt. Mater.* 9, 230 (1998).
- 11. T. Shirafuji, A. Kamisawa, T. Shimasaki, Y. Hayashi, and S. Nishino, *Thin Solid Films* 374, 256 (2000).
- Z. Ge, X. Zhang, J. Dai, W. Li, and Y. Luo, *Eur. Polym. J.* 45, 530 (2009); (b) Y. Kim, K. Chung, E. Lee, and Y. Seo, *J. Ind. Eng. Chem.* 14, 752 (2008).
- 13. S. Y. Cho and E. Kim, SPIE Proceeding 4991, 282 (2003).
- 14. S. Y. Cho and E. Kim, Mat. Res. Soc. Symp. 665, 339 (2002).
- 15. E. Kim, J. Park, S. Y. Cho, N. Kim, and J. H. Kim, *Etri J.* 25, 253 (2003).
- 16. D. J. Vyas, B. A. Makwana, H. S. Gupte, K. D. Bhatt, and V. K. Jain, J. Nanosci. Nanotechnol. 12, 3781 (2012).
- K. H. Lee, Y. K. Kim, and S. S. Yoon, *J. Nanosci. Nanotechnol.* 12, 4203; (b) L. Zhang, D. Zhang, S. Zhan, P. Yang, G. Yang, Z. Huang, and Y.-S. Lee, *Macromol. Res.* 20, 212 (2012).
- M. Suzuki, H. Kasai, T. Ishizaka, H. Miura, S. Okada, H. Oikawa, T. Nihira, H. Fukuro, and H. Nakanishi, J. Nanosci. Nanotechnol. 7, 2748 (2007).

- **19.** J. You, J. Kim, T. Park, B. Kim, and E. Kim, *Adv. Funct. Mater.* 22, 1417 (**2012**).
- **20.** S. N. Ali, S. Ghafouri, Z. Yin, P. Froimowicz, S. Begum, and M. A. Winnik, *Eur. Polym. J.* 44, 4129 (**2008**).
- B. Liu, X. Zhao, X. Wang, and F. Wang, J. Appl. Polym. Sci. 90, 947 (2003).
- 22. J. P. Jayachandran, H. A. Reed, Z. Hongshi, L. F. Rhodes, C. L. Henderson, S. A. B. Allen, and P. A. Kohl, J. Microelectromech. S. 12, 147 (2003).
- 23. V. L. Shannon and M. Z. Karim, Thin Solid Films 270, 498 (1995).
- 24. K. Tsukuma, N. Yamada, S. Kondo, K. Honda, and H. Segawa, J. Non-Cryst. Solids 127, 191 (1991).
- 25. D. Zhou, Y. Koike, and Y. Okamoto, J. Fluorine Chem. 129, 248 (2008).
- **26.** J.-M. Wang, L.-D. Wang, and L. Feng, *J. Appl. Polym. Sci.* 120, 524 (2011).
- 27. O. Ozel, T. Ozel, H. V. Demir, and D. Tuncel, *Opt. Express* 18, 670 (2010).
- 28. C. Wu, Y. Zheng, C. Szymanski, and J. McNeill, J. Phys. Chem. C 112, 1772 (2008).
- 29. R. Duggal, J. J. Shiang, C. M. Heller, and D. F. Foust, *Appl. Phys. Lett.* 80, 3470 (2002).
- **30.** K. Wang, J. Chen, W. Zhou, Y. Zhang, Y. Yan, J. Pern, and A. Mascarenhas, *Adv. Mater.* 20, 3248 (**2008**).
- **31.** C. Park, S. Seo, H. Shin, and E. Kim, *J. Korean Soc. Imaging Sci. Technol.* 18, 35 (**2012**).

Received: 24 July 2012. Accepted: 21 January 2013.

Delivered by Publishing Technology to: Florida State University, College of Medicine IP: 184.99.174.178 On: Fri, 06 Nov 2015 06:22:32 Copyright: American Scientific Publishers