※그림 2~4번 칼라인지 흑백인지 확인부탁드립니다.

Journal of Radiation Industry 6 (4) : 317~322 (2012)

The Preparation of a Thermally Responsive Surface by Ion Beam-induced Graft Polymerization

Chang-Hee Jung, Wan-Joong Kim, Chan-Hee Jung, In-Tae Hwang and Jae-Hak Choi*

Research Division for Industry and Environment, Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongeup 580-185, Korea

Abstract - In this study, the preparation of a temperature-responsive poly(N-isopropylacrylamide) (PNIPAAm)-grafted surface was performed using an eco-friendly and biocompatible ion beam-induced surface graft polymerization. The surface of a perfluoroalkoxy (PFA) film was activated by ion implantation and N-isopropylacrylamide (NIPAAm) was then graft polymerized selectively onto the activated regions of the PFA surfaces. Based on the results of the peroxide concentration and grafting degree measurements, the amount of the peroxide groups formed on the implanted surface was dependant on the fluence, which affected the grafting degree. The results of the FT-IR-ATR, XPS, and SEM confirmed that the NIPAAm was successfully grafted onto the implanted PFA. Moreover, the contact angle measurement at different temperatures revealed that the surface of the PNIPAAm-grafted PFA film was temperature-responsive.

Key words : Ion-beam, Graft polymerization, PNIPAAm, Contact angle

INTRODUCTION

The creation of stimuli-responsive surfaces has attracted a considerable attention owing to their biological applications including tissue engineering, biosensor, and drug delivery (Mendes 2008; Martien *et al.* 2010; Techawanitchai *et al.* 2011). Stimuli-responsive surfaces have been widely fabricated through a non-covalent or covalent introduction of smart polymers onto the substrate surface that can respond to external stimuli such as temperature, pH, light, solvent, electrical potential, or a combination thereof (Shirtcliffe *et al.* 2005; Yu *et al.* 2005; Heinz *et al.* 2008).

The surface grafting has been preferred owing to its advantages including the controllable introduction of the grafted chains onto a surface with a high density without affecting the bulk properties, and the long-term stability of the covalently-grafted chains (Cui *et al.* 1999; Uhlmann *et al.* 2006). Thus, stimuli-responsive polymers were introduced onto the surface of various substrates through a variety of surface-initiated polymerization methods using chemical initiators, UV-radiation, plasma treatment, and high-energy radiation (γ-rays or electron beams) (Spridon *et al.* 2012; Biazar *et al.* 2011).

Ion beam-induced graft polymerization is a fascinating method to introduce a thermally-responsive polymer on the surface of a substrate owing to its several advantages such as a surface-specific modification, no requirement of toxic chemicals such as an additional initiator or organic solvent, and good reliability and controllability (Hook *et al.* 2006; Ziauddin and Sabatini 2011). Thus, this method has been used in the formation of functional groups on a polymer surface suitable for electronic and biological applications (Yun *et al.* 2010; Hwang *et al.* 2011). In spite of these merits, the preparation of a thermally-responsive poly (N-isopropylacrylamide) (PNIPAAm)-grafted surface through ion beam-induced grafting has not been studied yet.

* Corresponding author: Jae-Hak Choi, Tel. +82-63-570-3062, Fax. +82-63-570-3090, E-mail. jaehakchoi@kaeri.re.kr

In this study, an eco-friendly and biocompatible method to generate a thermally-responsive surface through ion beam-induced grafting was described. The surface of a polymer film was modified through ion implantation and followed by surface graft polymerization under various conductions. The resulting surface was characterized in terms of the peroxide concentration, grafting degree, chemical structure, and morphology. Furthermore, the thermally-responsive behavior of the resulting films was demonstrated by measuring the water contact angle at different temperatures.

MATERIALS AND METHODS

Materials

Perfluoroalkoxy (PFA) films (100 μm thickness, Ashai Glass Co., Ltd.) were washed by sonication in acetone for 20 min and dried in a vacuum oven at room temperature overnight prior to use. N-isopropylacrylamide (NIPAAm, 97%), 1,1-dipheyl-2-picryhydrazyl (DPPH) were purchased from Aldrich Company and used without further purification.

The surface graft polymerization by ion implantation

The surfaces of well-cleaned PFA films were implanted with 150 keV H^+ ions at room temperature at various fluences ranging from 5×10^{14} to 1×10^{16} ions cm^{-2}. The pressure in the implanter's target chamber was 1×10^{-5} to 1×10^{-6} Torr. The ion beam current density was less than 1.0 μA cm^{-2} to prevent a thermal effect on the substrate. The resulting PFA films were stored in air for 24 h for further oxidation.

The implanted PFA films were put into glass tubes containing a 20 wt% aqueous solution of NIPAAm, and then purged with nitrogen gas for 30 min to remove oxygen. For graft polymerization, the tubes were placed in a constant temperature water bath at 62°C for 12 h. Afterward, the resulting films were taken out of the tubes and thoroughly washed with deionized water to remove the homopolymers. The resulting PNIPAAm-grafted PFA films were then dried under a vacuum at 50°C.

Surface characterization

The amount of peroxide groups generated on the PFA surface after ion implantation was measured using a well-known DPPH method described in the literature (Suzuki *et al.* 1986). Briefly, the implanted PFA substrates were immersed in a glass tube containing a DPPH solution in toluene with a concentration of 10^{-4} M. After purging with nitrogen, the glass tube was heated to 70°C and kept at that temperature for 5 h to decompose the peroxide groups formed on the surfaces. The amounts of DPPH molecules binding to the formed radicals were calculated from the difference in the absorbance at 520 nm between the original and residual DPPH solutions using an S-1100 UV-Vis spectrophotometer (Scinco Co., Ltd., Korea).

The grafting degree of the PNIPAAm grafted on the surface of the PFA substrates was determined using a Fourier transform infrared spectrometer (FT-IR) equipped with an attenuated total reflection (ATR) prism (FT-IR-ATR, Varian 640). As the base substrate was PFA, the characteristic absorption bands attributed to C-F asymmetric stretching vibrations in CF_2 groups were observed at about 1142 cm^{-1}. The absorption of amide carbonyl derived from NIPAAm grafts appeared at 1650 cm^{-1}. The peak intensity ratio of (I_{1650} /I_{1142}) was used to determine the graft density of PNIPAAm on the surface. The known amount of PNIPAAm was cast on the surface of the PFA film and used for a calibration curve (Akiyama *et al.* 2004).

The surface chemical composition of the control, implanted, and PNIPAAm-grafted PFA surfaces was investigated using an X-ray Photoelectron Spectrometer (MultiLab 2000, Thermo electron corporation, England) employing Mg-Kα radiation and the Advantage 3.70 program installed in the instrument was used to separate the XPS peaks in the C1s core level spectra. The applied power was 14.5 keV and 20 mA.

The temperature-dependant contact angles of the PNIPAAm-grafted PFA surfaces were measured by a sessile drop method using a Phoenix 300 contact angle analyzer (Surface Electro Optics Co.) equipped with a environmental chamber that can control the temperature within a range of 0 to 100°C.

The surface morphology of the control, implanted, and PNIPAAm-grafted PFA surface was investigated using a scanning electron microscopy (SEM, JEOL JSM-6390).

RESULTS AND DISCUSSION

The amounts of peroxide groups formed on the implanted

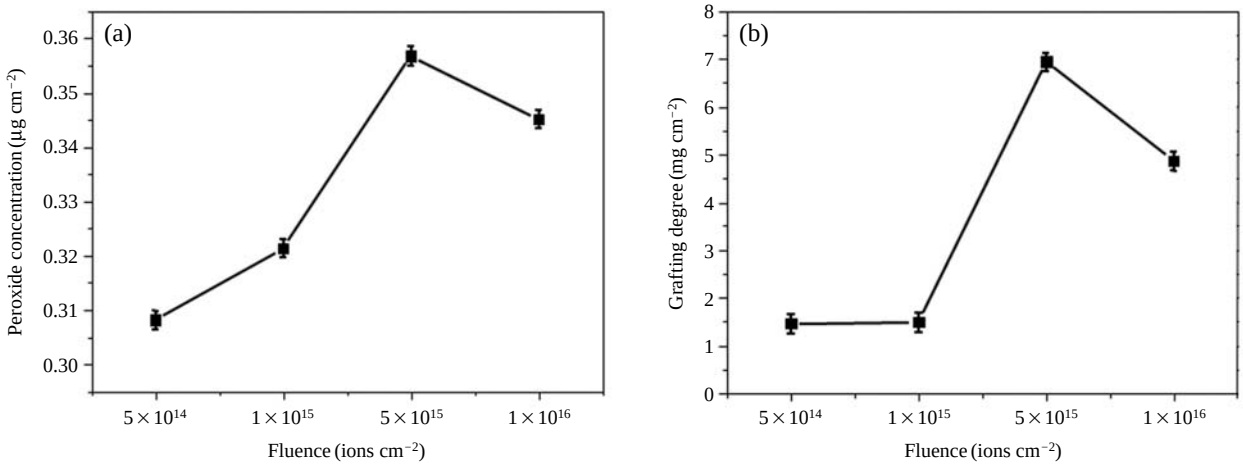

Fig. 1. The peroxide concentration (a) and grafting degree (b) as a function of the fluence.

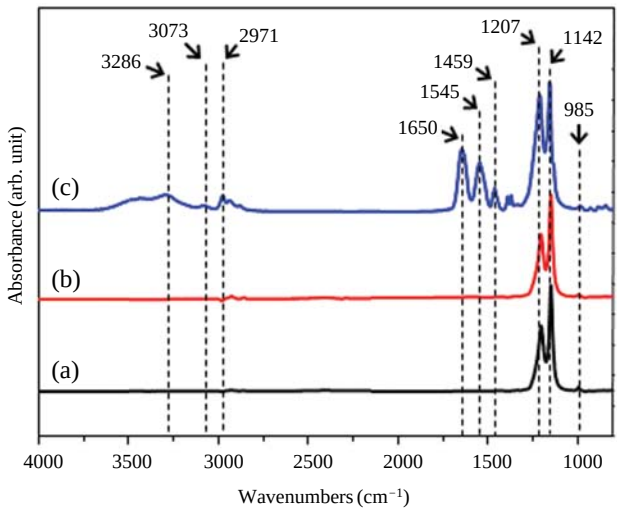

Fig. 2. FT-IR-ATR spectra of the control (a), implanted (b), and PNIPAAm-grafted PFA films (c).

PFA surfaces at different fluences were determined by a well-established DPPH method, and the results are presented in Fig. 1(a). The peroxide concentrations formed on the PFA surfaces increased with increasing the fluence to 1×10^{15} ions cm^{-2}, beyond which it decreased. This result indicates that the peroxide groups were effectively generated on the implanted surface at lower fluences through ion implantation-induced oxidation, but at fluences higher than 1×10^{15} ions cm^{-2}, the carbonization prevailed, resulting in a reduction of peroxide concentration (Cho *et al.* 2003). Furthermore, as shown in Fig. 1(b), the change in the grafting degree as a function of the fluence exhibited a similar tendency to the peroxide concentration. The highest grafting degree, 6.9 mg cm^{-2}, was obtained on the implanted PFA at a fluence of 1×10^{15} ions cm^{-2}, which exhibited the highest peroxide concentration. This result can be ascribed to the fact that the higher amounts of peroxide groups used to initiate the graft polymerization can generate a higher number of PNIPAAm chains on the PFA surface (Kim *et al.* 2006).

The surface chemical structure of the control, implanted, and PNIPAAm-grafted PFA films were analyzed using FT-IR-ATR and the results are shown in Fig. 2. The PFA film implanted at a fluence of 5×10^{14} ions cm^{-2} and PNIPAAm-grafted PFA film with a grafting degree of 6.9 mg cm^{-2} were used for this analysis. As shown in the control PFA spectrum of Fig. 2(a), the typical absorption bands attributed to the asymmetric and symmetric stretching of CF_2 groups in the PFA were identified at about 1142, 1207, and 985 cm^{-1}, respectively (Nasef 2001). As shown in Fig. 2(b), identical bands were observed in the spectrum of the implanted PFA without the formation of new bands corresponding to the oxidized species. On the other hand, as presented in Fig. 2(c), new characteristic bands assigned to the chemical structure of PNIPAAm appeared at 3286 and 1545 cm^{-1} for the secondary amide, 2971 and 1459 cm^{-1} for the aliphatic hydrocarbon, and 1650 cm^{-1} for the carbonyl group, respectively (Huilin *et al.* 2004).

The surface chemical compositions of the control, implanted, and PNIPAAm-grafted PFA films were investigated using XPS and the results are presented in Fig. 3. As shown in Fig. 3(a) and 3(b), in the case of the implanted PFA, the [O]/[C] atomic ratio increased with increasing the fluence to 1×10^{15} ions cm^{-2}, over which it decreased. In contrast, the

3(b)가 맞는지 확인해주세요!

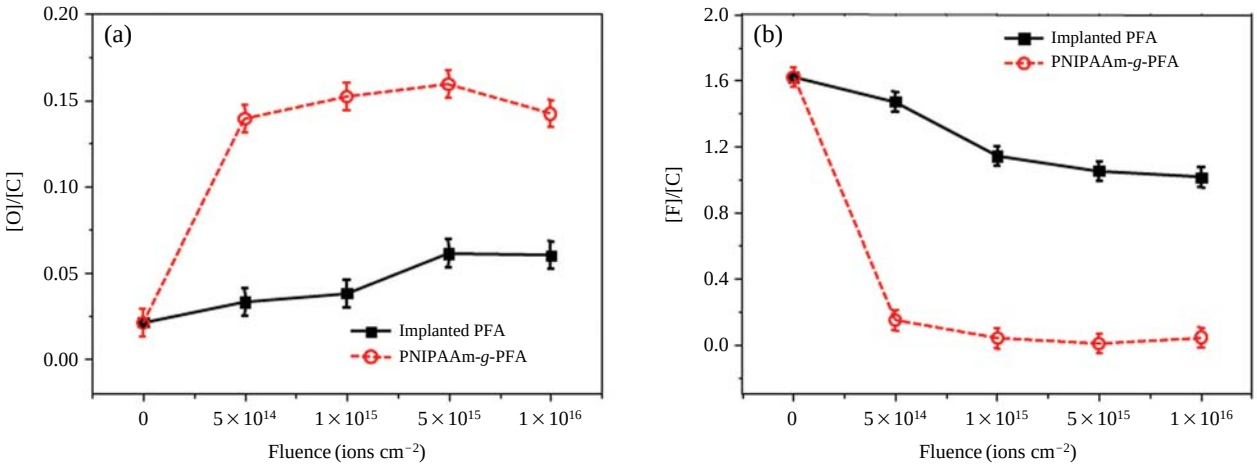

Fig. 3. [O]/[C] (a) and [F]/[C] ratio (b) of the control, implanted and PNIPAAm-grafted PFA films as a function of the fluence.

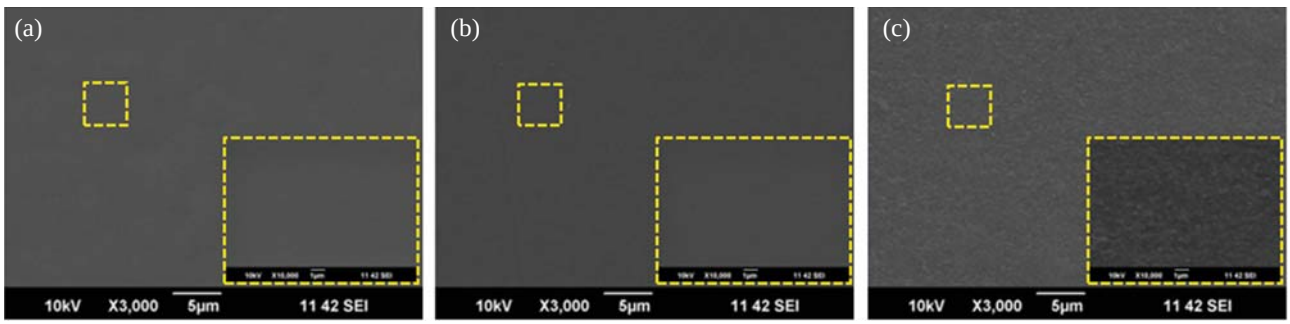

Fig. 4. SEM images of surface morphology of control (a), implanted (b), and PNIPAAm-grafted PFA films (c): the insets magnify the dotted rectangles in the respective images.

[F]/[C] atomic ratio exhibited an inverse tendency. For the PNIPAAm-grafted PFA, the [O]/[C] ratio further increased in comparison to that of the implanted PFA and in reverse, the [F]/[C] ratio further decreased as well. Furthermore, this change in the [O]/[C] and [F]/[C] atomic ratios was clearly dependant on the grafting degree. Therefore, the results verified that the PNIPAAm was successfully grafted onto the implanted PFA surface.

The surface morphologies of the control, implanted, and PNIPAAm-grafted PFA films were investigated using SEM observation, the results of which are shown in Fig. 4. The PFA film implanted at a fluence of 5×10^{14} ions cm^{-2} and PNIPAAm-grafted PFA film with a grafting degree of 6.9 mg cm^{-2} were used for this SEM observation. As shown in Fig. 4(a) and 4(b), the control and implanted PFA exhibited similar smooth surface morphologies meaning that the ion implantation did not bring about a morphological change in the PFA surface. On the other hand, as shown in Fig. 4(c),

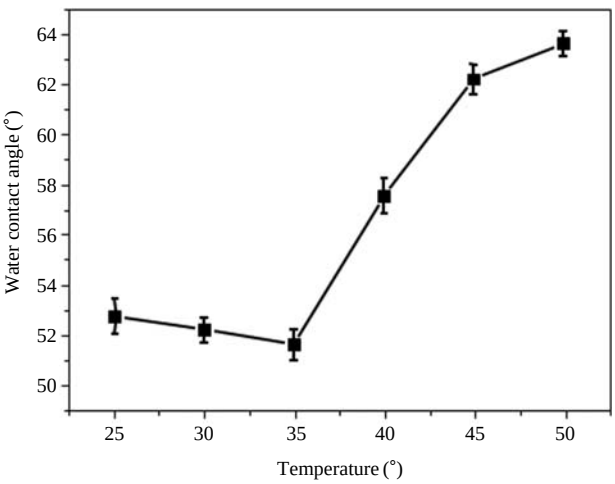

Fig. 5. Water contact angles of the PNIPAAm-grafted PFA films as the function of the temperature.

the surface morphology of the PNIPAAm-grafted PFA was much rougher in comparison to those of the control and im-

planted ones.

The thermally-responsive behavior of the PNIPAAm-grafted PFA surface was investigated by measuring the water contact angle at temperatures between 25 and 50°C, and the results are shown in the Fig. 5. The PNIPAAm-grafted PFA with a grafting degree of 6.9 mg cm^{-2} prepared through ion implantation at a fluence of 5×10^{14} ions cm^{-2} was used for the temperature-dependant contact angle measurement. Below 40°C, the surface exhibited contact angles of around 52°, but at a higher temperature, the contact angles increased to about 64°. This thermally-responsive behavior can be attributed to the temperature-dependant conformation transformation of the PNIPAAm (Balamurugan *et al.* 2003; Heinz *et al.* 2008).

CONCLUSION

In this research, a temperature-responsive PNIPAAm-grafted surface was successfully fabricated through ion beam-induced surface graft polymerization. Based on the results of the peroxide concentration and grafting degree measurements, the peroxide groups, used as an initiator for the surface graft polymerization, were effectively generated on the PFA surface through ion implantation and their fluence-dependant concentration determined the grafting degree of NIPAAm on the PFA surface. The results of the FT-IR-ATR, XPS, and SEM confirmed that the NIPAAm was successfully grafted onto the implanted PFA. Moreover, the contact angle measurement at different temperatures demonstrated that the surfaces of PNIPAAm-grafted PFA films were temperature-responsive. The resulting PFA films are applicable to a variety of biological applications.

ACKNOWLEDGEMENTS

This work was supported by the National Research Foundation Grant funded by the Ministry of Education, Science, and Technology, Korea (2012-M2A2A6013189).

REFERENCES

Akiyama Y, Kikuchi A, Yamato M and Okano T. 2004. Ultrathin Poly(N-isopropylamide) Grafted Layer on Polystyrene Surfaces for Cell Adhesion/Detachment Control. *Langmuir* **20**:5506-5511.

Balamurugan S, Mendez S, Balamurugan S, O'Brien MJ and Lopez GP. 2003. Thermal Response of Poly(N-isopropylacrylamide) Brushes Probed by Surface Plasmon Resonance. *Langmuir* **19**:2245-2549.

Biazar E, Khorasani MT and Daliri M. 2011. Cell Sheet Engineerin: Solvent Effect on Nanometric Grafting of Poly-N-isopropylacrylamide onto Polystyrene Substrate under Ultraviolet Radiation. *Int. J. Nanomedicine.* **6**:295-302.

Cho JS, Han S, Kim KH, Beag YW and Koh SK. 2003. Surface Modification od Polymers by Ion-Assisted Reaction. *Thin Soild Films.* **445**:332-341.

Cui FZ and Luo ZS. 1999. Biomaterials Modification by Ion-Beam Processing. *Surf. Coat. Technol.* **112**:278-285.

Heinz P, Bretagnol F, Mannelli I, Sirghi L, Valsesia A, Ceccone G, Gilliland D, Landfester K, Rauscher H and Rossi F. 2008. Poly(N-isopropylacrylamide) Grafted on Plasma-Activated Poly(ethylene oxide): Thermal Response and Interaction with Proteins. *Langmuir* **24**:6616-6175.

Hook AL, Thissen H and Voelcker NH. 2006. Surface Manipulation of Biomolecules for Cell Microarray Applications. *Trends Biotechnol.* **24**:421-477.

Huilin T, Carla E, Heitzman and Paul VB. 2004. Patterned Poly (N-isopropylacrylamide) Brushes on Silica Surfaces by Microcontact Printing Followed by Surface-Initiated Polymerization. *Langmuir* **20**:8313-8320.

Hwang IT, Kim DK, Jung CH, Lee JS, Choi JH, Nho YC, Suh DH and Shin K. 2011. Patterned Immobilization of Biomolecules on a Polymer Surface Functionalized by Radiation Grafting. *J. Nanosci. Nanotechnol.* **11**:4562-4566.

Kim JB, Ganesan, Yoo YS, Choi JH and Lee SY. 2006. Simple Patterning of Cell on Biocompatible Nonchemically Amplified Resist. *Macromol. Rapid Commun*. **27**:1442-1445.

Martien A, Cohen S, Wilhelm TS, Jan G, Marcus M, Christopher O, Manfred S, Gleb BS, Lgal S, Vladimir VT, Marek U, Francoise W, Stefan Z, lgor L and Sergiy M. 2010. Emerging Applications of Stimuli-Responsive Polymer Materials. *Nature Materials.* **9**:101-113.

Mendes PM. 2008. Stimuli-Responsive Surfaces for Bio-Applications. *Chem. Soc. Rev.* **37**:2512-2529.

Nasef MM. 2001. Effect of Solvents on Radiation-Induced Grafting of Styrene onto fluorinated Polymer Films. *Polymer Int.* **50**:338-346.

Shirtcliffe NJ, McHale G, Newton MI, Perry CC and Roach P. 2005. Porous Materials show Superhydrophobic to Superhydrophilic Switching. *Chem. Commun.* 3135-3137.

Spridon D, Curecheriu L, Dobromir M and Dumitrascu N. 2011. Synthesis of Poly(N-isopropylacrylamide) Under Atmos-

pheric Pressure Plasma Conditions. *J. Appl. Polym. Sci.* **124**:2377-2382.

Suzuki M, Kishida A, Iwata H and Ikada K. 1986. Graft Copolymerization of Acrylamide onto a Polyethylene Surface Pretreated with a Glow Discharge. *Macromolecules* **19**: 1804-1808.

Techawanitchai P, Tamamoto K, Ebara M and Aoyagi T. 2011. Surface Design with Self-Heating Smart Polymers for On-Off Switchable Traps. *Sci. Technol. Adv. Mater.* **12**:044609.

Uhlmann P, Ionov L, Nitschke M, Grundke K, Motornov M, Minko S and Stamm M. 2006. Surface Functionalization by Smart Coatings: Stimuli-Responsive Binary Polymer Brushes. *Prog. Org. Coat.* **55**:168-174.

Yun JM, Jung CH, Kim DK Hwang IT, Choi JH, Ganesan R and Kim JB. 2010. Photosensitive Polymer Brushes Grafted onto PTFE Film Surface for Micropatterning of Proteins. *J. Mater. Chem.* **20**:2007-2012.

Yu X, Wang Z, Jiang Y, Shi F and Zhang X. 2005. Reversible pH-Responsive Surface: From Superhydrophobicity to Superhydrophilicity. *Adv. Mater.* **17**:1289-1293.

Ziauddin J and Sabatini DM. 2011. Microarrays of Cells Expressing Defined cDNAs. *Nature* **411**:107-110.

Manuscript Received: October 7, 2012
Revised: November 17, 2012
Revision Accepted: December 10, 2012