Journal of Photopolymer Science and Technology
Volume 29, Number 3 (2016) 459－464 ©2016SPST

Cover-layering a Porous Polyimide Flexible Print Circuit with a Porous Polyimide Layer

Kentaro Taki*[1], Akira Mizoguchi[2], and Hiroshi Ito[3]

[1]*Advanced Reactive Lab, School of Natural System, College of Science and Engineering, Kanazawa University, 920-1192, Japan.*
[2]*Sumitomo Electric Industries, Ltd, 1-1-3, Shimaya, Konohana-ku, Osaka 554-002, Japan.*
[3]*Department of Polymer Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, Yamagata, 992-8510, Japan.*

Porous polyimide films are promising insulators for next generation electronic devices. Recently, we had developed a high-intensity UV exposure apparatus under a high-pressure CO_2 gas atmosphere for the production of porous polyimide films. In this study, the cover-layering process of a porous polyimide layer on two different types of flexible print circuits (FPCs) with insulation materials made of solid polyimide and porous polyimide was examined. Although a portion of the pores above and below the copper line of the FPC collapsed, a conformal porous polyimide layer could be formed on the FPC. Through-holes were formed on the porous polyimide film by a laser ablation technique. The surface of through-holes was electro-plated in a copper-plating solution bath. A portion of the pores on the film were filled with copper as the pores were inter-connected and the plating solution penetrated the pores. The results suggest that the pores should be isolated and firm for a cover-layering process with porous polyimide films for next-generation FPCs.
Keywords: copper plating, through-hole, porous film

1. Introduction

The increase in the data transmission speeds of smart phones and other hand-held communication devices necessitate next-generation substrate materials for high-throughput flexible print circuits (FPCs). In the field of microelectronics, it has been discerned that the signal attenuation becomes severe if high frequencies above several GHz are used to increase the data transmission speed. For improving the signal attenuation considering the substrate material of the FPCs, the relative dielectric constant, ϵ' and the loss tangent, $\tan \delta = \epsilon''/\epsilon'$, are to be reduced [1,2].

Porous polyimide (PI) is a promising material for next-generation FPCs because the relative dielectric constant can be reduced using numerous pores. The preparation of a porous PI film has been continuously studied by several researchers. Some of the studies have succeeded in creating ultra-low k porous material in which the relative dielectric constant is less than two [3-12].

However, most of the above mentioned studies have been limited to preparing the porous PI film and providing reports on the relative dielectric constant. Very few studies exist on building electrical circuits on the porous PI films.

Recently, we have developed a novel preparation process for the porous PI film employing a zwitterion-induced phase separation between a *tert*-amine methacrylate monomer and *N*,*N*-dimethylacetamide as a solvent [13]. The process was extended for preparing a 70 × 150 mm^2 sized film by building a new apparatus. A microstrip line of the FPC was formed on the porous PI film. The signal attenuation of the high-frequency signal was compared to a solid PI film. With

Received June 2, 2016
Accepted June 15, 2016

the same length, width, and height of the microstrip line for the porous PI and the solid PI, it was observed that the porous PI substrate could reduce the signal attenuation [14].

Although the preparation of the micro-strip line on the porous PI film was successful, there are several challenges for applications in real devices. Generally, an FPC consists of several layers and through-holes that electrically connect the layers. There is a concern that the porous structure would collapse if covered by another porous PI layer. Further, copper plating solution could permeate through the through-holes. Examining the preparation of the cover-layer for the porous PI and the copper plating through the through-holes in the porous PI film can be beneficial for understanding the methodology for usage in FPCs.

Thus, in this study, a porous PI layer was formed on two different FPCs, with a solid PI and a porous PI, respectively. Further, through-holes were prepared on the porous PI film and subjected to copper plating. The cross-section of the porous structure as well as the copper plating was observed by a field emission type scanning electron microscope (FE-SEM) at a low acceleration voltage without a metal coating.

2. Experimental

2.1. Porous polyimide film

A porous polyimide film was prepared using the high-intensity UV exposure apparatus under a high-pressure CO_2 gas atmosphere reported in previous studies [13, 14].

Pyromellitic dianhydride (PMDA) and 4, 4-diaminodiphenyl ether (ODA) with an *N*,*N*-dimethylacetamide (DMAc) type polyamic acid (PAA) solution were prepared by polymerization at 80 °C with nitrogen purging. The solid part of the solution was at 15 wt. %. Approximately 1.58 g (8.53 mmol) of a UV curable monomer, 2-(diethylamino) ethyl methacrylate (TCI, Japan), and 0.201 g (0.577 mmol) of a photoinitiator, diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure TPO, BASF), were added to 6.56 g of the PAA solution and stirred until a homogeneous solution was obtained.

The solution was cast on a smooth copper foil at 30 mm s^{-1} with a 200-μm gap baker film applicator on a hot-plate at 40 °C. The copper film on the hot plate was placed in the high-intensity UV exposure apparatus. The experimental condition was as follows: Briefly, the CO_2 dissolution time and pressure were 60 s and 6.5 MPa, respectively. The UV exposure time and intensity at 365 nm were 60 s and 80% of the maximum intensity, ~ 200 mW cm^{-2}, respectively.

The transformation from the precursor to a porous PI film was achieved by heat treatment in a nitrogen-flushed oven (DN610I, Yamato Scientific, Tokyo, Japan) using the following temperature gradients: (1) 40 °C for 120 min, (2) 3 °C/min to 110 °C for 60 min, and (3) 3 °C/min to 320 °C for 60 min under 20 L/min of nitrogen.

An FPC was prepared using the same procedure as in our previous study [14]. The surface of porous polyimide film was treated by UV light for enhancing the wettability of the plating solution. The film was then coated with a catalyst for an electroless nickel phosphine (Ni-P) plating. Further, the film was electro-plated in a copper plating solution for forming the ground plane. Now the porous PI film was sandwiched with the ground plane and the copper foil.

A dry-film resist was applied to the copper foil (not the electroplated side) of the porous polyimide. The pattern of the electrical circuit was exposed, and the circuit was developed. The development of FPCs of the porous PI was performed by MULTI, Japan and related companies.

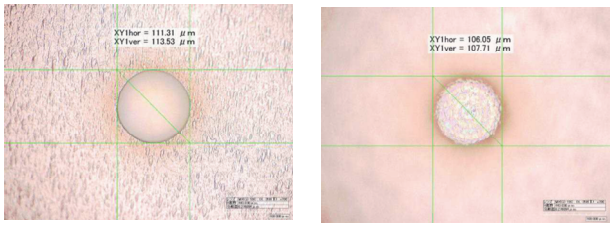
2.2. Lamination of the porous PI film

The porous polyimide layer was formed on the FPC by repeating the preparation of the porous PI film on the copper foil, described above.

2.3. Through-hole

A mask pattern of the through-holes was prepared by CO_2-laser ablation on a copper foil. The mask pattern was covered on the copper foil. CO_2-laser ablation was applied to the copper foil to strip off the porous film through the mask pattern at a relatively low power. Finally, a desmear treatment was applied for cleaning the pattern on the porous PI film.

CO_2-laser ablation was employed for making through-holes on the porous PI film in the same manner as on the FPC. The diameter of the through-hole was 100 µm. Fig. 1 shows the optical microscope images of a through-hole prepared by laser ablation. The diameter of the surface close to the surface of the porous film is *ca*. 112 µm, while that at the bottom is *ca*. 107 µm. The hole diameter is reduced from the top to the bottom gradually by laser attenuation.



(a) (b)

Fig. 1. Optical microscope images of the through-hole focused on the (a) top surface, (b) bottom surface.

2.4. FE-SEM observation

A cross-section of the specimen was obtained by an Argon ion beam cross section polisher (IB-09020CP, JEOL, Japan). Typically, the acceleration voltage was 6.0 kV, the emission current was 180 µA, and the operation time was 5 h.

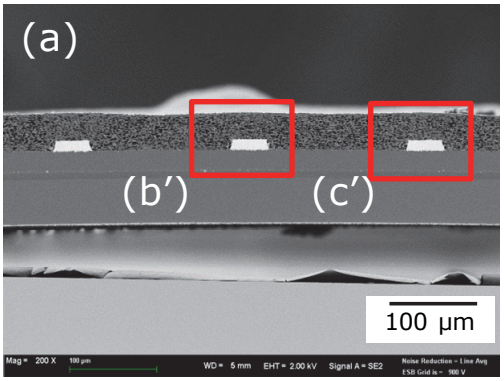
The cross-section of the specimen was observed by a field emission type scanning electron microscope (Ultra55, Carl Zeiss, German) without a metal coating. The acceleration voltage was 1 kV for SEM observation for avoiding a charge-up. The working distance was 5 mm.

3. Results and Discussion

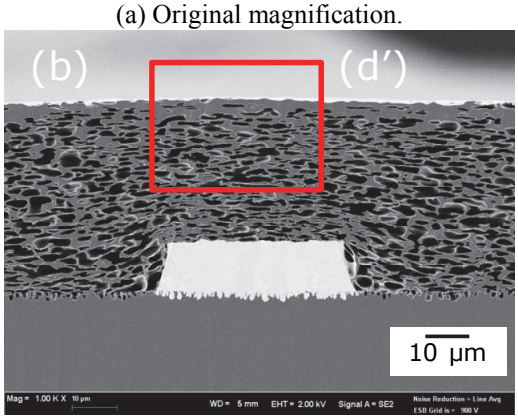
3.1. Lamination of the porous PI film

A porous PI layer was formed on the FPC in the apparatus. Fig. 2 shows the FE-SEM micrograph of the cross-section of the porous PI layer on the FPC.

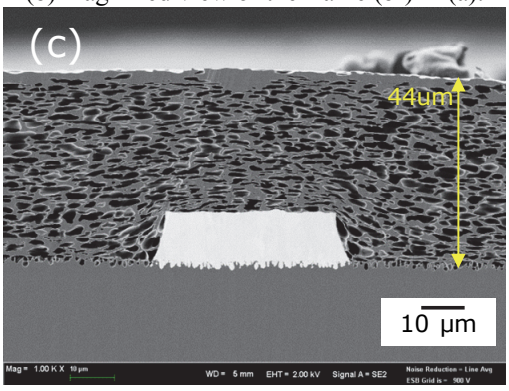
One of the challenges in reducing the relative dielectric constant by forming several pores on the film is reducing the thickness of the skin layer in which no pores exist. If the skin layer is too thick, the relative dielectric constant cannot be reduced as expected owing to the high-porosity in the core layer. As shown in Figs. 2 (b) and (c), the thickness of the skin layer is approximately less than 1 µm that is sufficiently small for reducing the relative dielectric constant.



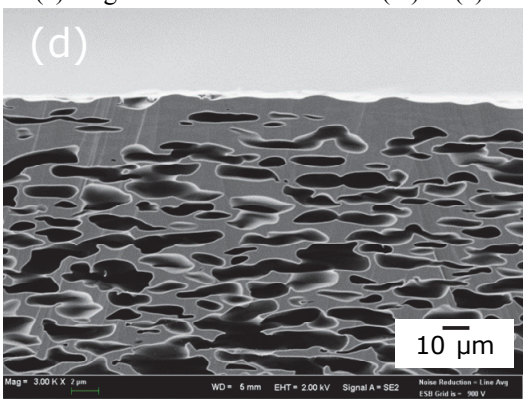
(a) Original magnification.



(b) magnified view of the frame (b') in (a).



(c) magnified view of the frame (c') in (a).



(d) magnified view of the frame (d') in (c).

Fig. 2. FE-SEM micrograph of the porous PI layer on the FPC. (a) Original magnification, (b) magnified view of the frame (b') in (a), (c) magnified view of the frame (c') in (a), (d) magnified view of the frame (d') in (c).

The porous PI layer covers the copper line of the FPC conformally. A portion of the pores had collapsed vertically because of the shrinkage during thermal imidization. The pore size distribution changes depending upon the distance from the copper line as shown in Figs. 2 (b) and (c): (1) the pores are collapsed vertically above the copper line, (2) large pores are observed just beside the copper line and (3) a relatively uniform pore size distribution is observed away from the copper line. The pores above the copper line collapsed because the copper line and the surface of the porous PI had squeezed the pores during thermal imidization.

Fig. 3 shows the FE-SEM micrograph of the porous PI layer on the FPC made of the porous PI film. As shown in Fig. 3 (a), the boundary of the porous PI films is observed clearly. In Fig. 3 (b), the pores above and below the copper line are collapsed in the vertical direction. There are gaps beside the copper line. In Figs. 3 (c) and (d), the gap is magnified. It was expected that the PAA solution would cover the copper line and no gaps would exist. The differences in the thermal expansion ratios of PI and copper had caused a thermal stress at the interface between the porous PI and the copper line. Eventually, the cover layer was peeled off and the gap was formed during thermal imidization.

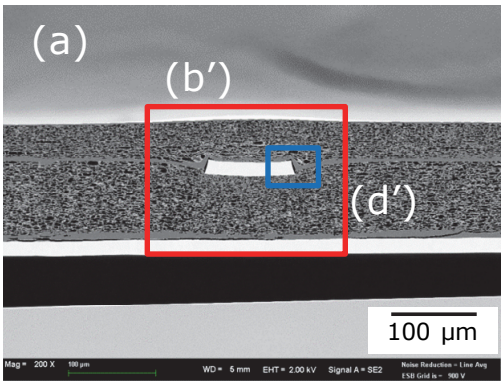
In Fig. 3 (d), the pores in the bottom layer are severely collapsed. The pores might have collapsed when the PAA solution was coated by a wire bar on the bottom layer or during the thermal imidization process.

3.2. Copper plating on the through-holes of the porous PI film

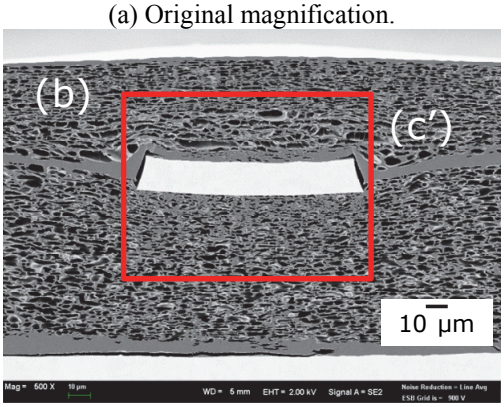
A layer of copper was deposited on the porous PI film by electro-copper plating. Fig. 4 shows the FE-SEM micrograph of the cross-section of the copper plated porous PI film with the through-holes.

As shown in Fig. 4 (a), copper plating adequately covers the top surface of the porous PI film. The left-side through-hole is well-covered, while in the right-side, the bottom of the through-hole is not covered. The plating was relatively unstable when examined owing to the limited trials.

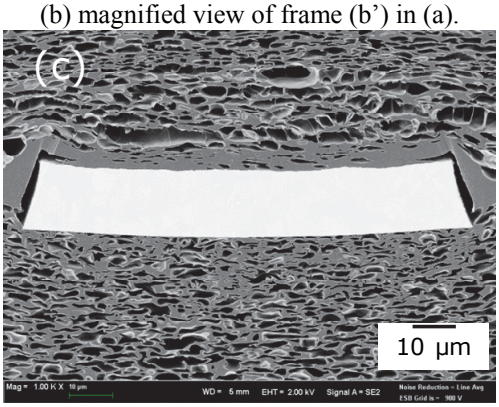
In Figs. 4 (b) and (c), a portion of the pores are filled with copper plating. The result of the element analysis is shown in Fig. 4 (d). Tables (i) and (iii) in Fig. 4(d) show that the indicated locations, "-¦-", are filled with copper as the weight percent of



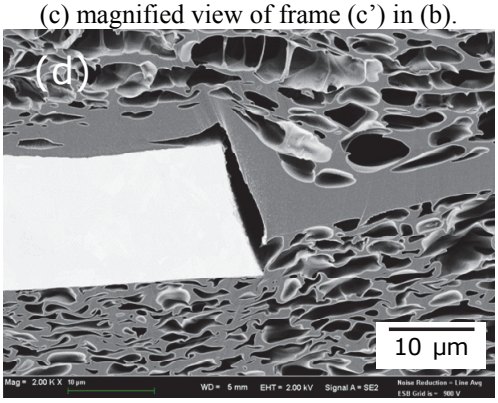
(a) Original magnification.



(b) magnified view of frame (b') in (a).

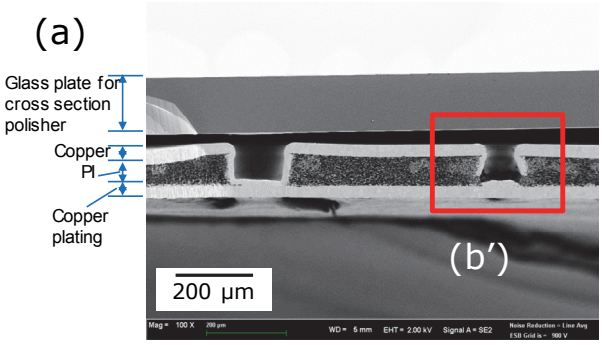


(c) magnified view of frame (c') in (b).

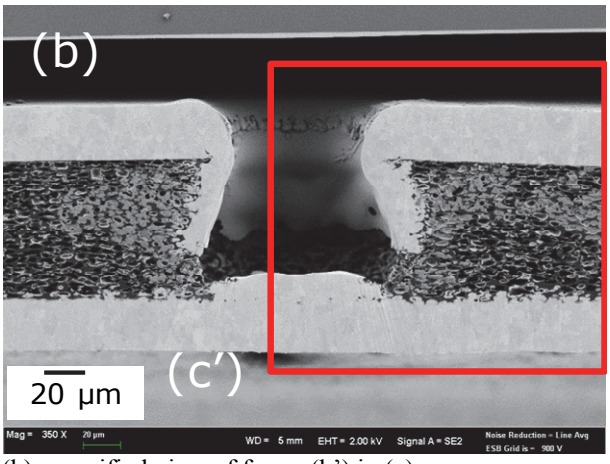


(d) magnified view of frame (d') in (a).

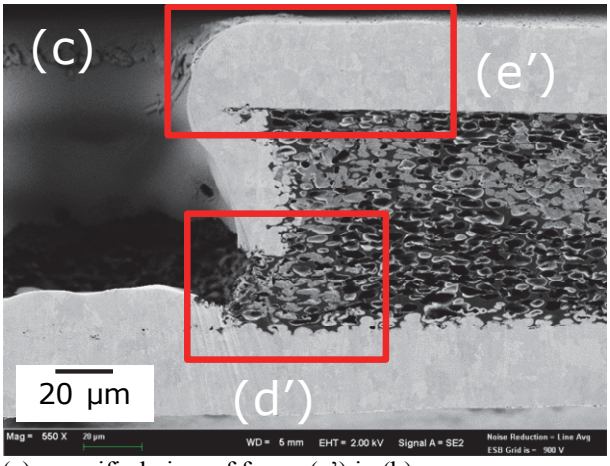
Fig. 3. FE-SEM micrograph of the porous PI layer on the FPC of the porous PI film. (a) Original magnification, (b) magnified view of frame (b') in (a), (c) magnified view of frame (c') in (b), (d) magnified view of frame (d') in (a).



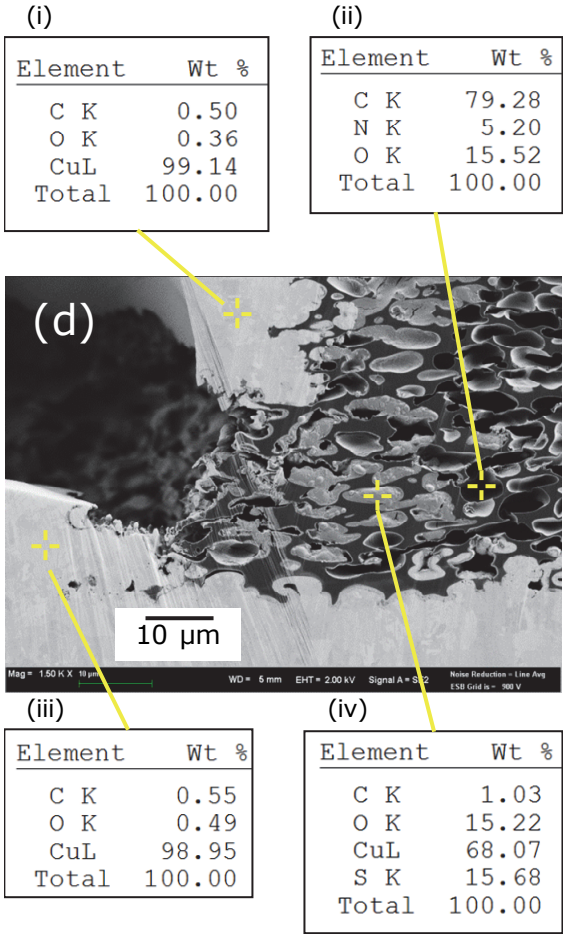
(a) Original magnification.



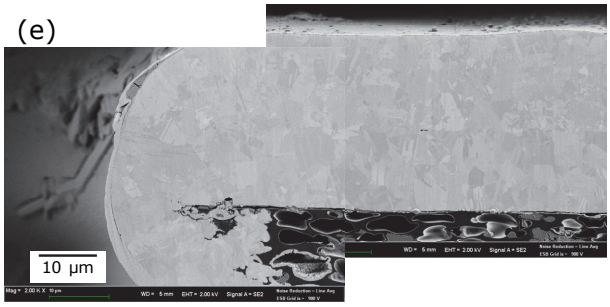
(b) magnified view of frame (b') in (a).



(c) magnified view of frame (c') in (b).



(d) magnified view and results of the element analysis in frame (d') in (c).



(e) magnified view of (e') in (c).

Fig. 4. Copper electro plating on a porous PI film and through-holes (a) Original magnification, (b) magnified view of frame (b') in (a), (c) magnified view of frame (c') in (b), (d) magnified view and results of the element analysis in frame (d') in (c), (e) magnified view of (e') in (c).

copper is larger than 98 wt%. Table (ii) represents a vacant pore and copper is not deposited in the pore. However, in the location indicated in table (iv), copper and sulfur are prominent, while carbon is less. It is evident from element analysis that the pore is filled with copper. The copper in the pore was formed during the electroless plating process. Some pores interconnect with each other, hence, the plating solution had permeated into the pores and a plating reaction had occurred. This result points out that the insulation of the porous PI film could be damaged by the electroless plating process.

It is imperative to form fully isolated pores for insulation. In our previous study, the interconnection of the pores could be reduced by increasing the pre-baking time [14]. Optimization of the pre-baking time for realizing an increase in the volume fraction of the pore (porosity) as well the resistance to the copper plating process should be investigated in future studies.

4. Conclusion

A porous PI layer was formed on two different FPCs made of solid PI and porous PI, respectively. Through-holes were prepared on the porous PI films and subjected to copper plating. The cross-section of the porous structure as well as the copper plating was observed by FE-SEM.

For the FPC with the solid PI, the pores above the copper line of the FPC collapsed in the vertical direction. Large pores existed beside the copper lines.

For the FPC made of porous PI, the pores above and below the copper line collapsed. A solid layer was formed in the boundary between the two porous PI layers. Gaps between the copper line and the solid layer were observed.

When the porous PI with the through-holes was copper plated, some of the pores were filled with copper because the pores were interconnected and the copper-plating solution permeated into the pores.

Although porous PI films are promising next generation substrate materials for FPCs, this study has revealed considerable challenges in practical applications. It is imperative to prepare isolated and firm pores in the PI films for overcoming these difficulties.

References

1. M. H. Weng, H. W. Wu, Y. K. Su, R. Y. Yang, C. Y. Hung, *Microwave Opt. Technol. Lett.*, **48** (2006) 1675.
2. H. W. Wu, Y. K. Su, R. Y. Yang, M. H. Weng, Y. D. Lin, *Microelectron. J.*, **38** (2007) 304.
3. B. Krause, K. Diekmann, N. F. A. van der Vegt, M. Wessling, *Macromolecules*, **35** (2002) 1738.
4. B. Krause, G. H. Koops, N. F. A. van der Vegt, M. Wessling, M. Wubbenhorst, J. van Turnhout, *Adv. Mater.*, **14** (2002) 1041.
5. A. Mochizuki, T. Fukuoka, M. Kanada, N. Kinjou, T. Yamamoto, *J. Photopolym. Sci. Technol.*, **15** (2002) 159.
6. Y. J. Lee, J. M. Huang, S. W. Kuo, F. C. Chang, *Polymer*, **46** (2005) 10056.
7. Y. Ren, D. C. C. Lam, *J. Electron. Mater.*, **37** (2008) 955.
8. M. A. Wahab, K. Y. Mya, C. B. He, *J. Polym. Sci., Part A: Polym. Chem.*, **46** (2008) 5887.
9. X. Y. Zhao, H. J. Liu, *Polym. Int.*, **59** (2010) 597.
10. S. Chisca, I. Sava, M. Bruma, *Polym. Int.*, **62** (2013) 1634.
11. S. Ma, Y. Wang, Z. Min, L. Zhong, *Adv. Polym. Tech.*, **32** (2013) 21358.
12. F. Lv, L. Liu, Y. Zhang, P. Li, *J. Appl. Polym. Sci.*, **132** (2015) 41480.
13. K. Taki, K. Hosokawa, S. Takagi, H. Mabuchi, M. Ohshima, *Macromolecules*, **46** (2013) 2275.
14. K. Taki, H. Ito, *J. Photopolym. Sci. Technol.*, **28** (2015) 747.