Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Surface-Grafting of Polyglutamate on Si Wafer Using Micro Contact Printing

Jonghyub Kim [a], Jaehyun Park [a], Seongyeol Lee [a] & Daewon Sohn [a]

[a] Department of Chemistry, Hanyang University, Seongdong-gu, Seoul, Korea

Version of record first published: 22 Sep 2010

To cite this article: Jonghyub Kim, Jaehyun Park, Seongyeol Lee & Daewon Sohn (2007): Surface-Grafting of Polyglutamate on Si Wafer Using Micro Contact Printing, Molecular Crystals and Liquid Crystals, 464:1, 211/[793]-216/[798]

To link to this article: http://dx.doi.org/10.1080/15421400601031017

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 211/[793]–216/[798], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601031017

Taylor & Francis
Taylor & Francis Group

Surface-Grafting of Polyglutamate on Si Wafer using Micro Contact Printing

Jonghyub Kim
Jaehyun Park
Seongyeol Lee
Daewon Sohn
Department of Chemistry, Hanyang University, Seongdong-gu, Seoul, Korea

Surface-grafting of poly(γ-benzyl-α, L-glutamate) (PBLG) on the 3-aminopropyl triethoxysilane (APS) pretreated silicone substrates was conducted by the monomer, γ-benzyl-L-glutamate N-carboxyanhydride (BLG-NCA) which was synthesized through the phosgenation procedure. PBLG, one of liquid crystalline polymers, micro-patterns were fabricated by micro-contact printing (μCP) and surface-grafting method. Then, PBLG patterns were characterized with electron microscopy (SEM), atomic force microscopy (AFM), infrared spectroscopy (FT-IR), Raman spectroscopy and polarized optical microscopy. α-helix conformation of PBLG was dominated on the patterned surface which was confirmed by FT-IR spectroscopy. From the polarizing microscope images, lyotropic liquid crystalline properties of the patterned surfaces were observed. The SEM and AFM images show that the height of PBLG patterns was 300 nm and line width was 15 μm. The interval between lines was about 5 μm.

Keywords: lyotropic liquid crystalline property; micro-contact printing; PBLG; surface grafting

1. INTRODUCTION

In recent years, ultra thin (from monolayer to 1 μm) organic films have been considerably focused for their great potentials in electronic and opto-electronical applications such as non-linear optics (NLO), liquid crystal displays (LCD), solar cells and biosensors. There have been

This work was supported by the research fund from ABRL program of KRF. J. Kim thanks the National R&D project for Nano Science & Technology in ITEP.

Address correspondence to Daewon Sohn, Department of Chemistry, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, Korea. E-mail: dsohn@hanyang.ac.kr

many efforts to bottom up control the thickness and the properties of these thin films, which are the key issues for their applications. The molecular orientation in thin films with respect to the substrate is very important for several applications. Since the oriented organic layers can exhibit optoelectronic and piezoelectric properties, they can be applied to electronic and opto-electronic devices.

Polyglutamate is a well known thermotropic and lyotropic liquid crystalline polymer which has α-helix conformation. In our experiments, poly(γ-benzyl, L-glutamate) was synthesized and grafted on the silicon wafer to generate the polymer brushes having rodlike characteristics. Polyglutamate can easily be synthesized by the ring-opening polymerization of N-carboxyanhydrides (NCAs) [1]. N-carboxyanhydrides were prepared by phosgenation of the corresponding L-glutamic acid esters [2–7]. The polymerization process was initiated with primary amines through the "amine mechanism" [8,9]. Most polymerizations are performed in polar solvents such as acetonitril, dioxane, and N,N′-dimethylformamide (DMF) in order to keep the formed polypeptide material in solution for a long time. In particular, at temperatures between $40 \sim 60^{\circ}$C, the DMF molecules prevent the aggregation of the α-helices structure. At the high concentration of the polypeptide, lyotropic liquid crystalline behaviors could be observed [10]. Aims of these works are making the patterned rodlike brushes and investigate the liquid crystalline behaviors on the silicon wafer surface, which could be used as opto-eletronical devices.

2. EXPERIMENTS

2.1. Preparation of Polyglutamate Thin Film on Si Wafer

Prepolymer, BLG-NCA, was synthesized with L-glutamate, γ-benzyl ester (BLG) and triphosgene. 2 g of BLG (0.08 mol) was added to 15 ml of THF under N_2 atmosphere, and then it was set on the reflux process. 1.5 g of triphosgene (0.05 mol) was added to 15 ml of THF. And it was moved to BLG/THF mixture by cannulation under N_2 atmosphere. Reaction was performed for 5 hrs and product was obtained by recrystallization method using n-hexane. Obtained product was performed rephosgenation for 5 hrs one more time.

A silicon surface was covered with patterned 3-aminopropyltriethoxysilane (APS) or 4-aminobutyltriethoxysilane (ABS) layer using soft lithography method. For the soft lithography method, patterned PDMS stamp was drenched with 0.5 mol initiator solution. Then, pretreated Si wafer (hydroxylated Si wafer) was covered with PDMS stamp for 2 hrs. The PDMS stamp was peel off, and initiated Si wafer was rinsed with toluene, acetone, and absolute ethanol to remove untethered initiator unit. At the beginning, 0.2 M of

BLG-NCA solution was prepared in DMF solution. A silicon wafer which covered with patterned APS or ABS layer was immersed into BLG-NCA solution for 5 hrs at 60°C. APS or ABS was used as an initiator for the polymerization processes. Any amine terminal organo-silane could be used. Temperature must be under 60°C. Decomposition of polymer started at over 60°C. At the end, a silicon wafer which covered with polyglutamates was rinsed by DMF and finally ethyl alcohol. BLG-NCA was characterized by FT-IR, in which α-helix structure of PBLG on Si was observed from no absorption peaks of β sheet conformation. Figure 1 presents the scheme for the surface grafting processes of polyglutamate on Si wafer.

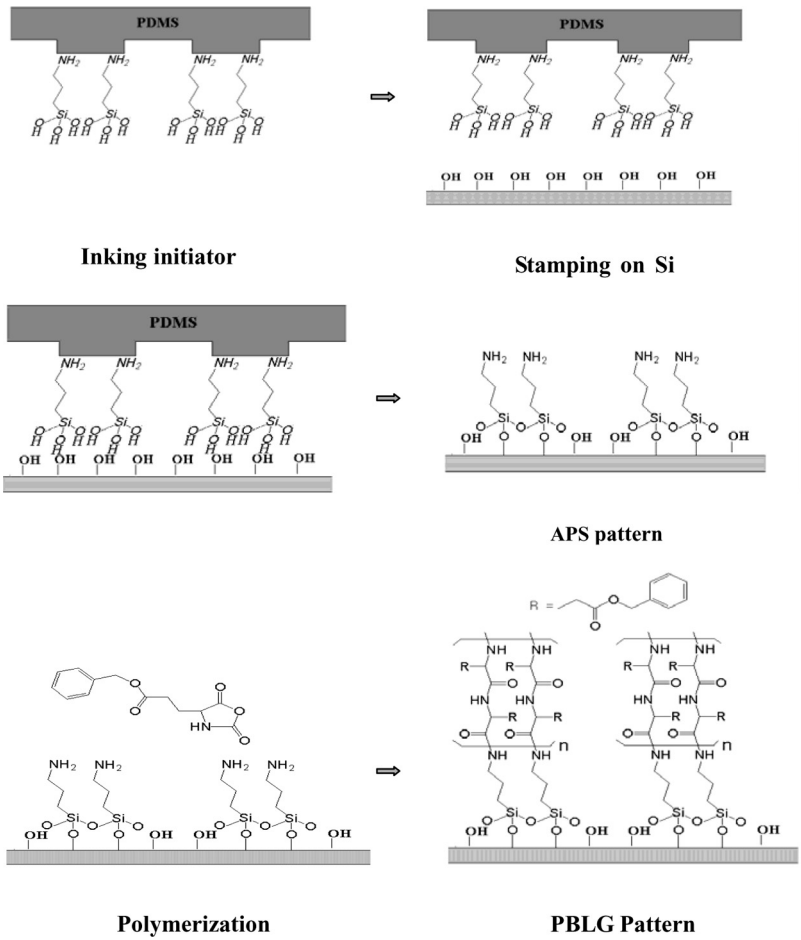

FIGURE 1 Scheme of surface grafting of polyglutamate on Si wafer.

2.2. FE-SEM Measurement

Samples were observed with FE-SEM (JEOL Ltd., JSM-6300). At an emission current 12×10^{-6} A and a probe current of 1×10^{-11} A. Samples were observed with non-conductive over-coating. Clear FE-SEM contrasts for the micropatterned APS and PBLG samples were obtained at 0.5 kV, $V_{acc,}$ where the contrast did not depend on V_{acc}.

3. RESULTS AND DISCUSSION

3.1. γ-benzyl, L-glutamate N-carboxyanhydride (BLG-NCA)

The BLG-NCA was synthesized by phosgenation of γ-benzyl L-glutamate (20 g, 0.084 mol) using triphosgene (10 g, 0.034 mol) in anhydrous THF. The crude product was purified by rephosgenation in the ratio of crude BLG-NCA/triphosgene (8/1; w/w). The BLG-NCA was recrystallized from a mixture of THF/n-hexane (1/5; v/v). The recrystallized product was filtrated and dried completely in vacuum. The weight of product was 19 g, 88% yield.

The stretching mode of carbonyl group always has two bands at $1830 \sim 1800\,cm^{-1}$. Conjugation moves the absorption to a lower frequency. On the other hands, the ring strain of cyclic anhydride moves the absorptions to a higher frequency. From the two absorptions at $1782\,cm^{-1}$ (anhydride band 2) and $1878\,cm^{-1}$ (anhydride band 1), it can be concluded that cyclic anhydride, NCA ring was formed. There are no absorptions at $1725 \sim 1700\,cm^{-1}$ which means no carboxylic acid residue exits. And no absorption of hydroxyl group was shown

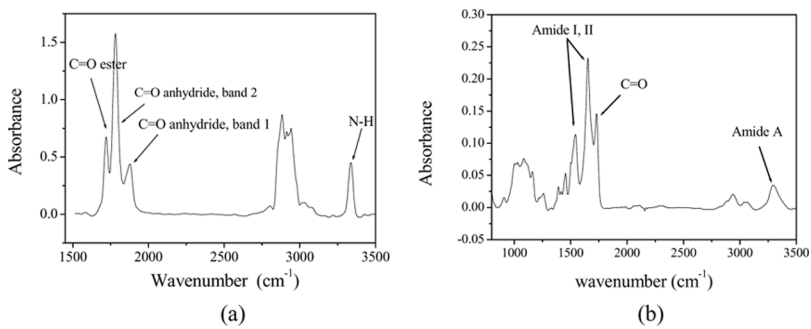

FIGURE 2 The FT-IR spectra. (a) BLG-NCA: two band of anhydride carbonyl group were shown at $1878\,cm^{-1}$ (band 1) and $1782\,cm^{-1}$ (band 2). (b) PBLG on Si wafer: there is no trace of β-sheet, amide A at $1630\,cm^{-1}$ and amide II at $1530\,cm^{-1}$. α-helix is the most stable conformation for PBLG molecule.

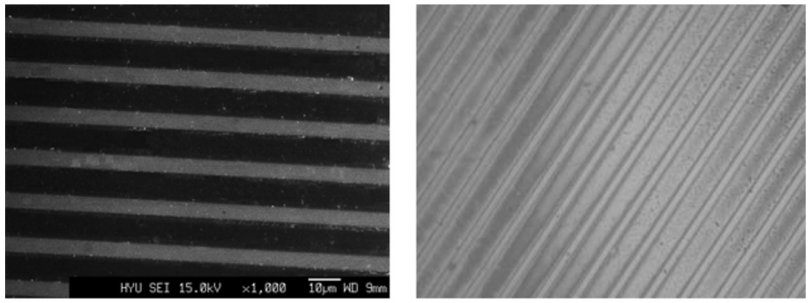

FIGURE 3 (a) FE-SEM image of PBLG pattern. The line width of PBLG patterns was 10 μm. The distance between the pattern lines was about 5 μm. (b) Polarizing Optical Microscope image of PBLG pattern on APS initiated Si wafer. Images were 500 magnifications.

in Figure 2(a). In Figure 2(b), we could verify the α-helix conformation of grafted PBLG. [11] amide A band and amide II band should be observed at 1630 cm^{-1} and 1530 cm^{-1} for the β-sheet conformation, but there is no these peaks.

Figure 3(a) shows FE-SEM image of patterned PBLG on Si wafer surface. After polymerization PBLG line width became 10 μm. Diffusion of APS and orientation of PBLG increase its width more than APS monolayer pattern. There are several small spots on PBLG pattern due to the APS residues.

The lyotropic liquid crystalline property of the PBLG pattern on the silicon wafers was investigated in DMF solvent system. A drop of DMF was added to the PBLG patterned surface and the solvent was evaporated for 30 min. at 50°C. It was observed by polarizing microscope and shown in Figure 3(b). When we rotate the angle of the polarizer, we could observe anisotropic image on the PBLG patterned surface.

PBLG pattern was also observed by AFM. Figure 4 shows the edge region is higher than the middle region. The edge region on the pattern is 500 nm tall and the middle region is 250 nm height. The edge effect covers around 3 μm width on both ends. We could obtain relatively uniform pattern with less than 5 μm width which has no edge effect.

4. CONCLUSION

We report the preparation and the characterization of PBLG pattern on Si wafer by surface-initiated grafting of polyglutamate, which could

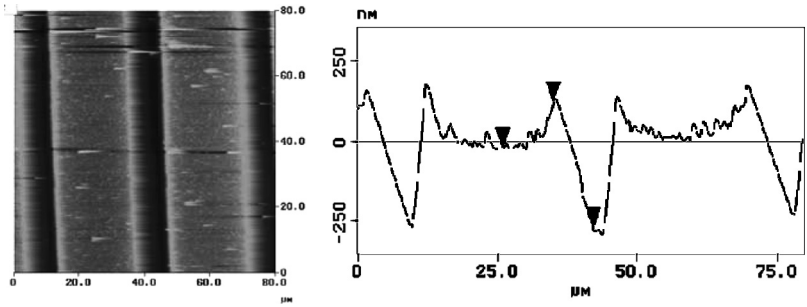

FIGURE 4 AFM images of PBLG pattern. The edge region on pattern is 500 nm tall and the center region is 250 nm.

be used as an optoelectronic device. The first step was to prepare primary amine functionalized Si surface with 3-aminopropyltriethoxysilane (APS) and to fabricate initiator patterns on the solid substrates by the micro-contact printing (μCP) method. The primary amine groups initiate the ring opening polymerization to produce patterned polyglutamate thin films on the Si surface.

The SEM and AFM images showed that the PBLG pattern on the Si wafer were prepared from $1 \sim 20\,\mu m$ width successfully. In cases, no other conformation than α-helix was detected by FT-IR spectroscopy. The lyotropic liquid crystalline behaviors were shown in polarizing microscope images due to the molecular orientation of PBLG.

PBLG has been known as liquid-crystalline materials, and soft lithography method has been used as the tool in designing of electronic circuit and optoeletronical devices.

REFERENCES

[1] Leuchs, H. (1906). *Ber. Dtsch. Chem. Ges.*, *39*, 857.
[2] Daly, W. H. & Poché, D. (1988). *Tetrahedron Lett.*, *29*, 5859.
[3] Wilder, R. & Mobashery, S. (1992). *J. Org. Chem.*, *57*, 2755.
[4] Dorman, L. C., Shiang, W. R., & Meyers, P. A. (1992). *Synth. Commun.*, *22*, 3257.
[5] Kricheldorf, H. R. (1990). In: *Models of Biopolymers by Ring-Opening Polymerization,* Penczek, S. (Ed.), CRC Press: Boca Raton, FL.
[6] Bamford, C. H. & Block, H. (1962). The polymerization of alpha-amino acid N-carbonic anhydrides. In: *Polyamino Acids, Polypeptides, and Proteins,* Stahmann, M. A. (Ed.), University of Wisconsin Press: Madison.
[7] Deming, T. J. (2000). *J. Polym. Sci., Part A: Polym. Chem.*, *38*, 3011.
[8] Wessely, F. (1925). *Z. Physiol. Chem.*, *146*, 72.
[9] Waley, S. G. & Watson, J. (1949). *Proc. R. Soc, A*, *199*, 499.
[10] Block, H. (1983). *Poly(γ-benzyl-L-glutamate) and Other Glutamic Acid Containing Polymers,* Gordon and Breach Sci. Publishers: New York.
[11] Fong, B. & Russo, P. S. (1999). *Langmuir*, *15*, 4421.