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# Notes

## Stable Patterning of Sensory Agarose Gels Using Inkjet Printing

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### Introduction

Recently, hydrogels are used as platform materials in biological research and medical systems. Hydrogels have also been applied as components in sensors[1] and drug release.[2] A multitude of techniques such as softlithography,[3] photolithography,[4] nanolithography,[5] and inkjet printing[6] have been used to form hydrogel patterns. Hydrogels are hydrophilic polymers and they are organized owing to van der Waals interactions, hydrogen bond, covalent bond, or physical entanglement. These materials often show significant swelling capability in water or biological fluids. The three-dimensional (3-D) network is usually maintained in swelled hydrogel states.

Micro/nano fabrication of biological materials into useful structures is an emerging technology which is valuable in molecular genetics, regenerative medicine, and other biological science. Inkjet printing has been described as a good candidate for formation of 3-D structures and patterns of bio-materials and conductive inks. Inkjet printing technique can print letters as well as patterns of complicated structures without loss of printing materials at higher speed and lower cost. Another significant advantage is its compatibility with various substrates which are nonflexible or flexible. In addition, small amount of materials can be deposited on the desired location of the substrate leaving negligible contamination by non-contact printing. The hydrogels used in inkjet printing has been numerously reported including alginate, chitosan, and gellan gum. However inkjet printing using agarose is still unknown.

Moreover there are a large number of operational parameters to be optimized when jetting hydrogel-based fluid.[7] Drop-on-demand inkjet printing called piezo inkjet printing (PIJ) has been much useful being capable of jetting a wide range of materials upon its mechanical action. In this contribution we developed a strategy for well-defined hydrogel-based pattern and its application by integrating characteristics of PIJ and agarose materials of ultra low gelling temperature (ULGT).

Polydiacetylene (PDA) supramolecules have been intensively investigated due to their unique stimuli-responsive color-changing properties against various environmental perturbations.[8] Thereby, we produced various letters which are recognizable with naked eyes by incorporating color-changing PDA in printed hybrid gel patterns.

### Experimental

**Materials and Instruments.** ULGT agarose with gel point 8~7 °C was purchased from Aldrich. 10,12-pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals. Deionized (DI) water (18 MΩ·cm) was used as a solvent. Ammonium hydroxide (28~30%, Aldrich) was used to react with PCDA-embedded ULGT agarose gel pattern. piezoelectric technology based on an inkjet printer (Omnijet 200, Unijet Korea) was used for patterning of ULGT agarose gel and PCDA-embedded ULGT agarose gel.

**Preparation of ULGT Agarose Gels Solution.** ULGT agarose was dissolved in heated deionized water at 90 °C. Various weight percentages of agarose in gels (0.1%, 0.2%, 0.4%, and 0.6%) were also fabricated.

**Preparation of PCDA Vesicle-Embedded ULGT Agarose Gels.** The carboxyl-terminated monomer PCDA was dissolved in chloroform. The solvent was evaprated to form thin dry film on the surface of a test tube by stream of $N_2$ gas and deionized water added to the test tube containing thin dry film. The resultant solution was stirred in a thermostat (RW-0525G, Jeio Tech, Korea) at 80 °C for 15 min to be dispersed well and sonicated (Sonic dismembrator 550, Fisher Scientific, USA) for 15 min. To remove the titanium particle of sonicator tip and monomer aggregates, the solution was filtered through a polytetrafluoroethylene (PTFE) membrane having pore size of about 0.8 μm. Filtered solution was stored in a refrigerator at the temperature of 4 °C for over 4 h. ULGT agarose (0.1%) was dissolved in heated PCDA vesicles solution (1 mM).

**Patterning of ULGT Agarose Gels and PCDA-Embedded ULGT Agarose Gels Using Inkjet Printer.** The PCDA vesicles-embedded ULGT agarose gel solutions were injected into the cartridge equipped with a nozzle of 50 μm. Jetting parameters such as voltages (V) and pulse widths affecting how the ink is jetted out of the nozzle head were optimized by

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