

Polymer Network on Optical Fiber Core

S. Kazakov

Department of Chemistry and Physical Sciences, Pace University
861 Bedford Road, Pleasantville, NY, USA, skazakov@pace.edu

ABSTRACT

The ultimate goal of the research is to fabricate a cylindrical polymer network (hydrogel) on the side-surface (not the distal end) of an optical fiber core and characterize spectroscopically its swelling/de-swelling ability in response to different stimuli. This paper demonstrates that an optical fiber with open core connected to a spectrometer is an apparatus for polymerization and analytical device in one. Kinetics of photopolymerization induced by the light passing through the fiber showed that evanescent waves scattered on the successively formed polymer layers leads to a cylindrically cross-linked polymer film around the fiber core. Surprisingly, the thickness of the hydrogel layer could be significantly greater than the depth of evanescent field penetration out of the fiber. Another unexpected observation was that, in the course of shrinking, the temperature sensitive poly-N-(isopropylacrylamide) hydrogel layer supported by fiber core absorbed the light of different spectral composition. Thus prepared cylindrical polymer network of nanometer size is a prerequisite for a supported 2D-single macromolecule. Based on a light-sensitive polymer cross-linked around a fiber core, is an optically pumped organic laser as well as optically controlled drug-release systems can be designed.

Keywords: cylindrical polymer network, optical fiber, evanescent wave polymerization, swelling/de-swelling.

1 INTRODUCTION

The idea of a hydrogel/optical fiber assemblage was employed for decades for fiber-optic chemical and biochemical sensors [1]. The unique property of hydrogels is their volume changes in response to environmental stimuli. Responsive hydrogel produces microbending in fiber and/or absorbs evanescent tail of the propagating light in fiber [2]. Hydrogel matrix serves as container for sensing ligands adsorbed onto, entrapped into or covalently bound to supporting matrices [3]. Hydrogel spots were polymerized on fiber distal ends by direct light [1,4]. Hydrogel was deposited on side-surface of a fiber core by spreading a polymer followed by cross-linking [17].

In this paper we put forth an idea of initiating polymerization by evanescent field in the vicinity of side-surface of optical fiber core to form and support a cross-linked polymer matrix (Figure 1). Evanescent waves have already been employed for spectroscopic detection in fiber-optic sensors [1]. However, to the best of my knowledge,

there are no reports on photopolymerization by evanescent waves in cylindrical configuration.

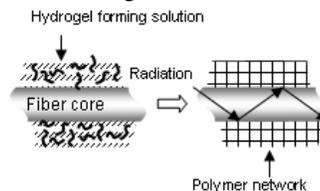


Figure 1: Photopolymerization in the vicinity of an optical fiber core using the evanescent waves.

Such a cylindrical hydrogel film is of great potential for the future applications, not limited to sensors. Keeping in mind that hydrogels exhibit both liquid-like and solid-like behavior [6], the cylindrical polymer matrices can interface between living matter (cells, organelles, and their liquid media) and inorganic electronic and spectroscopic probes (microchips). So, methods for preparation of the supported cylindrical hydrogels of different thickness are in demand.

In the course of the propagation of electromagnetic radiation inside the optical fiber, a portion of the electric field, which penetrates out of the fiber core (evanescent field), is used for initiation of polymerization in the surrounding hydrogel-forming medium. The depth of penetration of the evanescent wave, d , is the distance at which the intensity of the electric field has decayed to $1/e$ of that at the interface. Typically d is about few tenth of λ . The evanescent wave can interact with molecules located within the depth of penetration. The evanescent wave can be absorbed or can excite molecules around the area of a fiber core exposed for polymerization. Polymer network formed is not covalently bound to fiber side-surface. It is a kind of “cylindrical sock” on fiber core. Its thickness depends on the total and relative concentrations of monomers, cross-linker, initiator; spectral composition and power of light, and polymerization time.

Detection of the hydrogel film on the side-surface of fiber core is a challenge. We suppose that if the thickness of the hydrogel film changes in the course of hydration or with variation of external stimuli (in this work, temperature), the transmission spectrum of the fiber can vary. Thus, polymer matrix swelling/shrinking, if recorded by a spectrometer, is an evidence of hydrogel film formation on a fiber core.

The main objective of this work is to develop reproducible methods for polymerization by evanescent waves and detection and characterization of the cylindrical polymer network on side-surface (not distal end) of an optical fiber core.

2 EXPERIMENTAL SECTION

2.1 Materials

Monomer (*N*-Isopropylacrylamide, NIPA), cross-linker (*N,N'*-methylenebisacrylamide, MBA), and photoinitiator (2,2-diethoxyacetophenone, DEAP) were purchased from Aldrich (Milwaukee, WI). All chemicals were used as purchased. Water was purified by Milli-Q (Millipore). To synthesize a temperature-responsive poly(*N*-isopropylacrylamide) (PNIPA) hydrogel on a side surface of the fiber core, 20 mL of the following hydrogel forming solution were prepared in water: *N*-isopropylacrylamide (5 wt %), cross-linker (MBA, 0.5 wt %), and photoinitiator (DEAP, 0.5 wt%).

2.2 Optical Fiber, Reactor-Container, and Polymer Clad Removal

A SMA-SMA ending fiber cord (0.5 m) was made of a plastic clad silica optical fiber (BFH48-600, Thorlabs Inc., Newton, NJ) with a high OH content to provide transmission in UV and visible spectral ranges. A core diameter (600 μm) and numerical aperture (0.48) were selected to maximize the light intensity collected into the fiber under optimal length of the sensing area for fiber core. Thus, a 4-cm-long BFH48-600 fiber provides a path length of about 1.6 μm for an evanescent wave with the 365 nm wavelength. Based on this estimations the reactor-container has been designed (Figure 2).

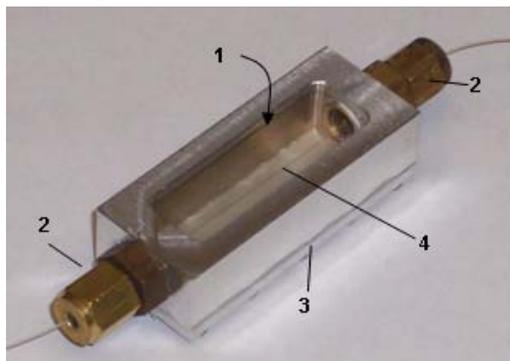


Figure 2: The reactor-container: (1) reservoir containing a polymerizable formulation (~12 mL), (2) sealing gaskets, (3) removable bottom cover, (4) area of fiber core without cladding exposed to a hydrogel-forming solution.

The fiber cladding was removed by a burning method using a propane or butane burning torch. The surface of fiber core free of polymer cladding thoroughly cleaned with isopropanol, distilled water, and finally, compressed air to remove any carbonization. The quality of the surface was controlled under an optical microscope.

2.3 Instrumentation

The effect of radiation intensity and wavelength on the hydrogel film formation by evanescent wave photopolymerization was examined using a 200 W Hg-Xe lamp (Newport Corporation). The UV light was focused with a condenser on SMA905 ending fiber which transmits the light through collimating lenses and bandpass filter to the BFH48-600 fiber cord. The intensity of light transmitted through the fiber was recorded in the course of polymerization by a fiber optic spectrophotometer (USB4000-UV-VIS, Ocean Optics, Inc.) with CCD array, which allows for simultaneous recording the spectrum range from 180 to 900 nm. SpectraSuite software was used to record, treat, and store radiation, transmittance and absorption spectra in a 1 sec time interval.

Digital Optical Microscope (DC3-163-PH, Microscope World, CA) with Imaging Software (Motic Images 2000, Motic Group, Ltd.) was used to measure the diameter of the bare fiber core and thickness of the cylindrical polymer network (hydrogel) on the fiber core after polymerization. This microscope was equipped with a CCD camera. To detect and characterize hydrogel film on fiber core after polymerization or during swelling/de-swelling, a QX3 microscope was used as well.

To provide a temperature control ($\pm 0.1^\circ\text{C}$), the reactor-container was placed into a temperature isolating box. A temperature sensor was dipped into the reactor-container nearby the fiber core. Transmission or absorption spectra were saved when temperature stabilizes on a certain level.

3 RESULTS

3.1 Hydrogel Film on Fiber Core



Figure 3: Optical micrographs (x10) of (a) bare fiber core on air, (b) hydrogel film on the fiber core on air after polymerization and washing, and (c) the same hydrogel film as for (b) dried overnight.

Figure 3a shows a fiber core on air before polymerization. After the hydrogel forming solution was injected to the reaction chamber in an amount to cover completely the fiber core, the UV light was allowed to pass through the fiber. Figure 3b clearly demonstrates that hydrogel film was synthesized around the fiber core after two hours of its exposition to UV light passing through. A blue glitter along the hydrogel cylinder shows that a portion of light passing through the fiber core penetrates outside as evanescent waves which scatter within the hydrogel film.

Figure 3c shows that the intensity of light scattered inside the same film but dried overnight is much higher than that in a wet state.

The average thickness of the film has been estimated using Motic Image Analysis program to be $\sim 175 \mu\text{m}$ in wet state, $\sim 60 \mu\text{m}$ after 6 hours of drying, and $\sim 30 \mu\text{m}$ after overnight drying on air.

3.2 Hydrogel Film Swelling: Dry-Wet Transition

Thus formatted on fiber core, PNIPA hydrogel film was washed in deionized water for 3 days and dried on air for 120 hours at room temperature. To examine the kinetics of hydrogel swelling in the course of film hydration, a Deuterium-Tungsten Halogen light source (DT-MINI-2, Ocean Optics) was connected to the one end of the fiber core with hydrogel film fixed in the reaction chamber, where as the Fiber Optic Spectrometer (USB4000) was connected to the other end. The time course of integral intensity of light passing through the fiber core with dried hydrogel film on it, is shown in Figure 4. Arrow indicates the moment of water injection into the reaction container. Sample was measured at room temperature.

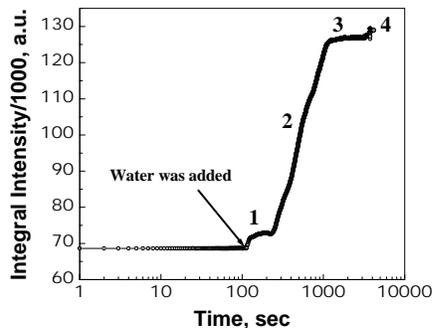


Figure 4: Integral intensity of light passed through the fiber core covered with dried PNIPA hydrogel film as a function of time in the course of hydration.

According to Figures 3a and 3b, one can expect a drastic decrease in scattering when dried hydrogel swells during water uptake, so that transmittance of the fiber increases. Therefore, Figure 4 reflects the kinetics of swelling of the hydrogel film on fiber core in the course of its hydration. The time log-scale was applied to distinguish different steps of the swelling. A “bump” (1) indicates the interval when water penetrates into the polymer network without pronounced swelling. During the interval (2) polymer network swells with a relatively high rate. It looks like the process (2), as well as the other two, (3) and (4), contains not only one step. These preliminary observations should be evaluated in details, yet, but what has been already demonstrated clearly that an optical fiber with open side surface of its core connected to a spectrometer is a perfect analytical device to study polymer network swelling/de-swelling kinetics.

3.3 Collapse of Hydrogel Film on Optical Fiber above LCST

In this section, we aim at studying the volume phase transition of the PNIPA hydrogel film at the so-called Lower Critical Solution Temperature (LCST). Hydrogel-polymer networks swollen in water are soft and gentle materials. Various external stimuli, such as changes in temperature, electric field, pH, etc., can control gel swelling (volume). Such gels belong to the group of responsive gels. Particularly, first order (collapse) volume phase transition in hydrogels induced by a change of temperature is of a great importance in applications [6]. At collapse, the volume of the gel changes from 10 to 1000 times from expanded state (at low temperatures) to collapsed state (at high temperatures). When temperature increases above LCST, a microphase separation of water in swollen gel occurs (due to polymer-water incompatibility). This leads to the formation of a heterogeneous structure and affects the mechanical and optical properties of the gels. While the mechanical properties are mostly influenced by swollen gel matrix, the optical properties are influenced mostly by droplets of excluded phase.

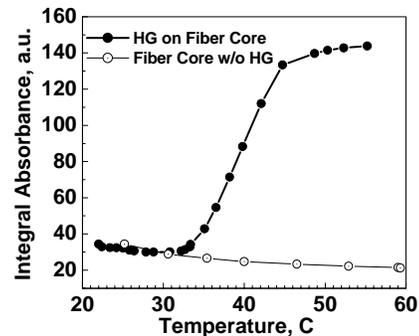


Figure 5: Temperature dependence of integral absorbance in PNIPA hydrogel film on optical fiber core in comparison with that in fiber core without a hydrogel.

The use of an optical fiber with open side surface of its core connected to a spectrometer can provide novel information on the spectral composition of an evanescent field scattered/absorbed within the medium in the vicinity of the fiber core surface.

Completely swollen hydrogel film on fiber core was equilibrated at certain temperature in the reactor container filled with distilled water. The integral absorbance (200 – 900 nm) was measured at each temperature using the same scheme as described in section 3.2. Figure 5 shows that absorption/scattering of evanescent light inside the PNIPA hydrogel film begins to increase at $\sim 32 \text{ }^\circ\text{C}$. This value is in good agreement with the transition temperature (T_c) known for PNIPA hydrogels from literature [7]. As a control experiment, the absorbance in the bare fiber core without any hydrogel has been measured to illustrate that changes are attributed to the collapsing hydrogel layer.

3.4 Spectrum of Light Scattered/Absorbed within Collapsed Hydrogel Film

Spectral composition of light scattered/absorbed in the collapsed polymer networks was not previously available experimentally. An experimental scheme proposed in this study exploits an optical fiber with open side surface of its core connected to a spectrometer with CCD array to allow one of recording the absorption spectra of the hydrogel/fiber assembly in the whole range of wavelengths for each temperature. The results are summarized in Figure 6. The most astonishing fact is that the spectral range of absorption depends on temperature, widening with the temperature increase above T_c . At temperatures higher than 55°C, absorption was observed in the whole range from 200 to 900 nm.

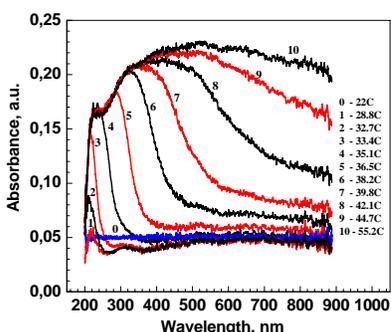


Figure 6: Temperature variations of absorption spectra of the fiber core covered by the cylindrical temperature-sensitive hydrogel (PNIPA).

This process is reversible, reflecting the reversibility of the volume phase transition. Below T_c , absorption decreases with temperature rise, just in accord with the temperature dependence of the fiber core absorption (cf. Figures 5).

4 DISCUSSION AND CONCLUSIONS

In this paper we have introduced a new method for polymerization of a cylindrical polymer network on side-surface (not distal end) of an optical fiber core by evanescent waves. The synthesis of a temperature sensitive polymer network of poly(*N*-isopropylacrylamide) around fiber core is described. Due to scattering of evanescent waves on the newly formed polymer microstructures, the polymerization can be initiated relatively far from the surface of fiber core, and the thickness of the cylindrical hydrogel film can be much greater than the depth of evanescent field penetration out of the fiber, which is typically about few tenth of wavelength. The swelling kinetics of thus prepared hydrogel was examined in the course of film hydration. One major new result obtained with these measurements that was not previously available is the observation of the absorption of the light of different spectral composition within a collapsing hydrogel at

different temperatures, namely: above the temperature of volume phase transition T_c , the hydrogel supported by fiber core begins to absorb/scatter the light in ultraviolet region, herein, the spectral range of absorbed light expands more and more to the visible and farther to the near infrared domains while temperature rises. While the detailed evaluation of these two unexpected results is still ongoing, the preliminary interpretation for both observations is based on the same phenomena known as Evanescent Wave scattering [8] and Mie scattering spectroscopy [9].

Finally, it was shown that an optical fiber connected to a spectrometer is an apparatus for polymerization and analytical device in one, which permits to shape, vitrify, and characterize a formed hydrogel film.

These results lead to an improved insight into collapse of these polymer materials and new practical applications of the fiber/smart hydrogel ensemble. For example, a stimuli-sensitive hydrogel film on a fiber core can tune optical properties of the optical fiber, or vice versa, light passing through the fiber can switch collapsed/swollen states of the polymer network.

This work was financially supported in part by Pace University (Dyson College of Arts and Sciences, Summer and Scholarly Research Funds). Acknowledgement is made to the Donors of the American Chemical Society/Petroleum Research Fund for partial support of this research (PRF grant # 44161-GB5).

REFERENCES

- [1] M. Mehrvar et al., *Analytical Sciences*, 16, 677, 2000; O.S. Wolfbeis, *Anal. Chem.*, 76, 3269, 2004; J. Yang et al., *J. Chin. Chem. Soc.*, 49, 677, 2002; F.J. Steemers, D.R. Walt, *Microchimica Acta*, 131, 99, 1999.
- [2] W.C. Michie et al., *Optics Letters*, 20, 103, 1995; A.P. Russell, K.S. Fletcher, *Anal. Chim. Acta*, 170, 209, 1985; R. Hyspser, H.J. Wierzba, *SPIE Proceedings*, 3054, 145, 1997.
- [3] W.A. Wyatt et al., *Anal. Chem.*, 59, 2272, 1987; L. Li, D.R. Walt, *Anal. Chem.*, 67, 3746, 1995; P. Hartman, W. Trettnak, *Anal. Chem.*, 68, 4512, 1996.
- [4] B.G. Healey, D.R. Walt, *Anal. Chem.*, 67, 4471, 1995.
- [5] Z. Ge et al., *Anal. Chem.*, 65, 2335, 1993.
- [6] R.S. Harland, R.K. Prud'homme (Eds.) *Polyelectrolyte Gels: Properties, Preparation, and Applications*, American Chemical Society, Washington, DC, 1992; N.A. Peppas, *Hydrogels in Medicine and Pharmacy*, CRC Press, Boca Raton, FL, 1987.
- [7] S. Kazakov et al., *Macromolecules*, 35, 1911, 2002.
- [8] Hung-JenWu et al., *Langmuir*, 24, 13970, 2008.
- [9] R. Trutna et al., *NSTI-Nanotech 2008*, 1, 835, 2008.