

## **In situ dynamic polymerization monitoring using silanized tilted fiber Bragg gratings**

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*Tilted fiber Bragg gratings (TFBGs) provide a convenient way to measure the surrounding refractive index by monitoring cladding modes variations in their transmitted spectrum. The presence of the core mode resonance combined to their small dimensions yield temperature-insensitive in situ refractometers that can be used to follow a chemical process in real time. In this work, we demonstrate that TFBGs can be used into a polymerization medium to track the growth of the polymer film by monitoring the evolution of the cladding mode resonances due to a surrounding refractive index change onto the surface of the silica fiber.*

### **Introduction**

There is a need for in-situ techniques to monitor on-substrate polymerization processes [1], mainly for thickness and quality monitoring. Contrary to most techniques that require taking sample from the polymerization medium for further analysis, optical fiber sensors allow direct in situ monitoring. In that context, Shevchenko et al have used gold-coated TFBGs for polyelectrolyte coatings monitoring on gold substrate by tracking the surface plasmon resonance [2]. In our work, we directly realize the polymerization process on the glass surface of TFBGs.

As they couple light towards the fiber cladding, TFBGs present cladding modes resonances that are sensitive to the SRI (Surrounding Refractive Index) in a range between 1,30 and 1,45 [3,4]. Tracking the evolution of these resonances (both in amplitude and in wavelength) gives information about the SRI.

In this paper, we analyze the growth of polyDMAEMA brushes (polydimethylaminoethylmetacrylate) grafted on the fiber silica surface [5]. The brushes were synthesized using the “grafting from” method by preparing a SAM (Self-Assembled Monolayer) of the initiator (chlorosilane in this case) and growing polymer chains by ATRP (Atom Transfer Radical Polymerization) process, which constitutes a controlled/living polymerization.

### **Experiments**

Experiments were conducted on TFBGs manufactured into hydrogen-loaded singlemode optical fiber by means of a 1095 nm uniform phase mask and a frequency-doubled Argon-ion laser emitting at 244 nm. The phase mask was tilted in the plane

perpendicular to the incident beam. To ensure strong couplings to cladding modes characterized by an effective refractive index close to the one of water (1,33), an external tilt angle of  $6^\circ$  was chosen.

Prior to work on optical fiber, the ATRP was optimized using silica planar substrate and the polymerization kinetics was studied by ellipsometry, yielding the evolution of the thickness as a function of time, as depicted in Fig. 1. The polymerisation process is described in the following.

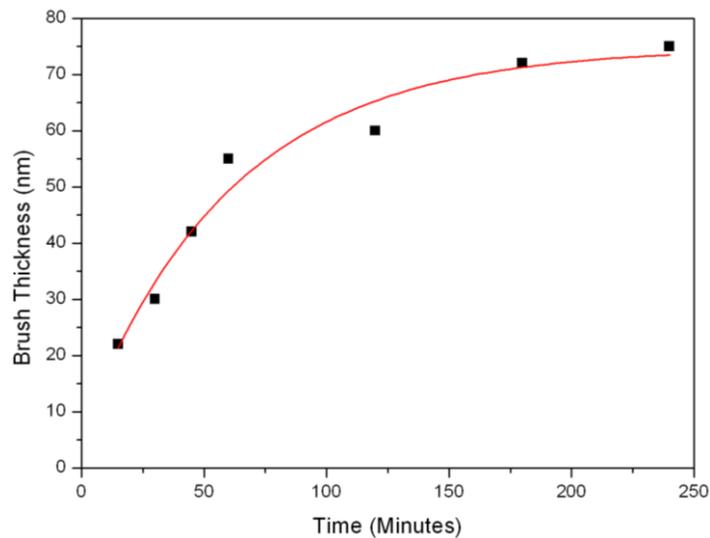


Figure 1: ATRP kinetics of DMAEMA on silica planar substrate (thickness vs time).

As expected, the growth of the chains is exponential and saturates around 70 nm after ~ 3 hours. This growth induces a change of the mean refractive index surrounding the fiber, which can be tracked against time through the monitoring of the amplitude spectrum evolution of TFBGs. For that purpose, we use an optical source covering the C+L bands and an optical spectrum analyzer, as shown on the sketch of the experimental setup (Fig. 2).

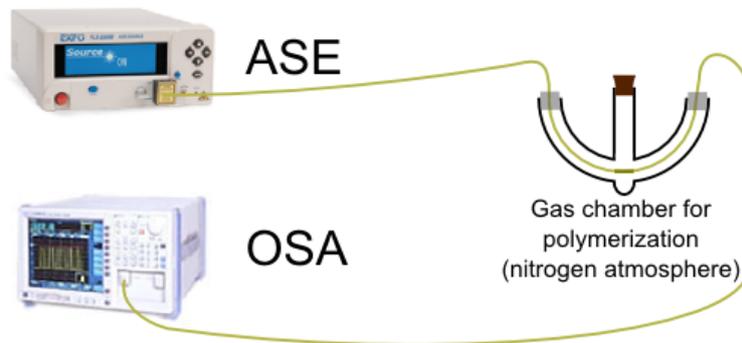


Figure 2: Sketch of the experimental set-up

The synthesis of the polymer requires the following steps. Firstly, fibers are put into an UV-ozone oven in order to activate the surface hydroxyl functions. This step is essential

to have the formation of the self-assembled monolayer (SAM) of initiators. The silanization (formation step of the SAM) is realized in vapor phase.

After that, the monomer is prepared, stabilization agents are removed and the catalytic compounds are dissolved into the reaction solvent.

Before pouring the different reagents into the reactor, a particular attention is put on the elimination of oxygen, which can react with the reagents, affecting dramatically the polymerization process. The whole vessel is also covered by aluminum foil in order to isolate the system from ambient light.

The monomer solution and the solvent with catalytic compounds are poured into the vessel, where the gratings have been previously placed, and the solution is slowly stirred during 4 hours at room temperature.

## Results

During the polymerization process, some cladding mode resonances change in amplitude, which testifies their sensitivity to the growth of the polymer chains. We focus on the five most sensitive resonances (called modes 1 to 5), as shown in Fig. 3. These modes extend in the range 1550-1558 nm. Fig. 3 presents the transmitted spectrum at two moments during the polymerization: at the beginning after 3 minutes and when the polymerization process is finished after 60 minutes. The most sensitive mode is the third one and is characterized by an amplitude variation of ~3 dB. Thanks to the cladding mode relationships [3], we estimate that the effective refractive index of this mode is close to 1.41. As a consequence, the refractive index of the polymer brush is also foreseen around that value.

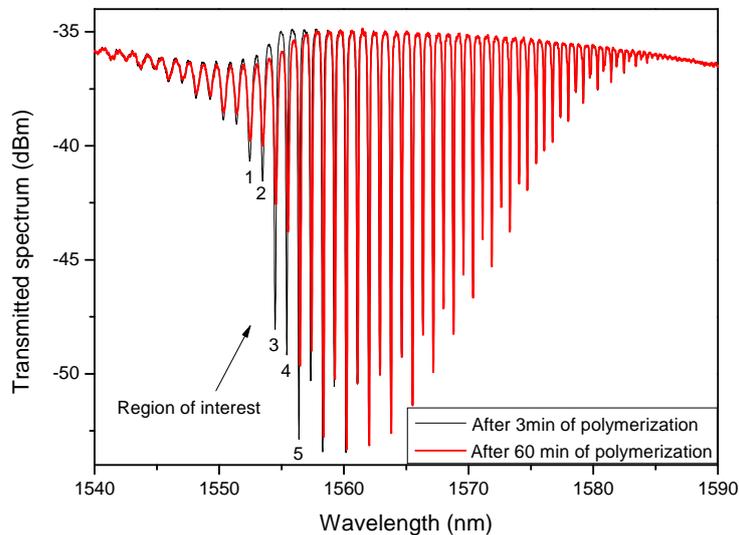


Figure 3: Cladding mode resonances spectrum of a  $6^\circ$  TFBR at two different moments during the polymerization process.

Tracking these modes as a function of time yields the results of Fig. 4 that shows a monotonic behavior up to ~ 40 minutes, corresponding to a brush thickness of ~40 nm. This is different from the results presented in Fig. 1. We believe that this discrepancy

results from a difference of growth kinetics between the flat substrate and the cylindrical shape of the optical fiber [2].

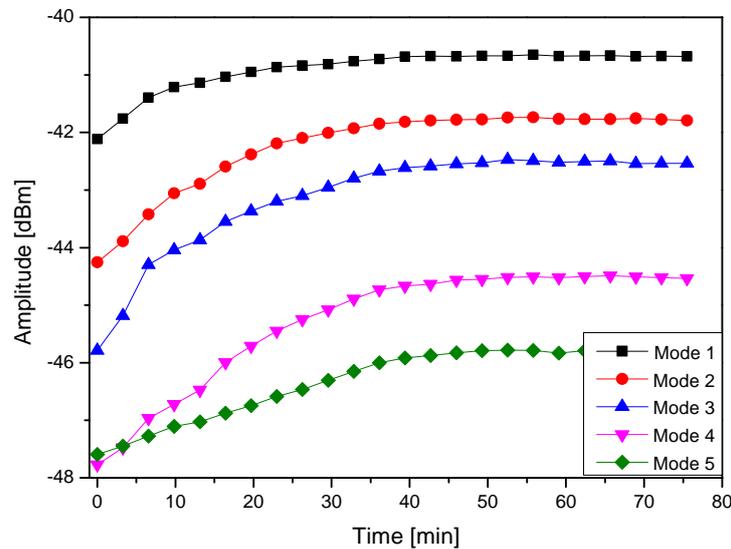


Figure 1: Tracking of cladding mode resonances of interest during the completed polymerization process of DMAEMA.

## Conclusions

We have demonstrated the possibility to monitor a polymerization process occurring at a surface using tilted fiber Bragg gratings. This can be observed due to the fact that the mean refractive index around the fiber increase during the formation of the polymer brushes. Further investigations will be lead to understand the possible difference between the polymerization kinetic on a flat substrate and on an optical fiber.

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