# Photografting of silica monoliths dedicated to nano liquid chromatography

**Sarah HADJ-CHIKH**

## Introduction

Miniaturization of chromatographic systems, i.e. reduction of the column diameter, was developed to decrease the consumption of solvents in order to reduce the economical and environmental impacts. The classical particulate stationary phases are not adapted. In this context, monolithic silica capillary phases synthesized in-situ in capillaries were developed.
The monolithic stationary phase was synthesized by the sol-gel process. It presents a continuous and homogeneous structure permitting to reach high efficiency on long columns. A scanning electron microscopic image of a capillary column with 70 µm i.d. is shown in Figure 1.
Nevertheless, to use this support in reversed-phase chromatography, it is necessary to modify its surface with hydrophobic groups. That's why an innovative process was developed: photografting. It consisted to irradiate with UV light the monolith impregnated with a solution of a monomer having an alkyl chain and an initiator. The aim of this work was first to study the photografting of monoliths previously silanized with reactive functions with alkyl chains; then to test their performance in reversed-phase liquid nano-chromatography.

## Experimental methods

The polymerization mixture was obtained by weighing proper amounts of:

- Benzoin methyl ether (BME), the initiator
- Tetrahydrofurane, the solvent
- Lauryl acrylate, the monomer

After mixing these compounds, the polymerization mixture was loaded in the transparent capillary column using a pressurized device. Then, the column was plugged with rubber stoppers and irradiated with a 365 nm UV light for indicated amounts of time. After that it was rinsed with tetrahydrofurane in order to remove any excess reagent.
Finally, the monolithic column was tested in reversed phase using UV detection at 214nm. The column was evaluated with a mixture of thiourea and pentylbenzene using a mobile phase acetonitrile-water (80/20).

## Results

The main characteristic of the studied monolith was the retention factor which has to increase with the photografting efficiency. Various synthesis formulations were tested changing the monomer concentration and the irradiation time. The results obtained are included in Table 1.
The procedure 1 showed that the irradiation time didn't really affect the performance of photografted capillaries: tripling the time of the exposition of the monolith increases the performance of 10% only. As can be seen in the procedure 2, an improvement in column retention properties was achieved at higher monomer concentration in the polymerization reaction mixture. Indeed, multiplying by two the percentage of monomer, the retention factor was gone up 20%. Besides, a second successive grafting in the same condition of the reference procedure showed an increase of 30% (procedure 3).

**Figure 1 : SEM Photography of a silica monolith synthesized in a fused silica capillary**

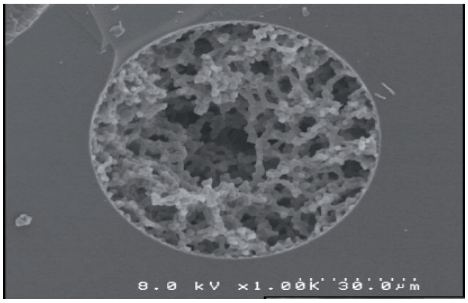

**Table 1 : Retention factors obtained after photografting**

| Procedures P | % Monomer | % BME | Irradiation Time | Retention factor |
|---|---|---|---|---|
| *Reference* | *37%* | *0,3%* | *20 mn* | *1.16 ± 0.01* |
| P1 | 37% | // | 1h | 1.27 ± 0.01 |
| P2 | 60% | // | 20 mn | 1.41 ± 0.01 |
| P3 (2nd successive grafting) | 37% | // | 20 mn | 1.48 ± 0.01 |

## Conclusion

The initial results showed very promising performance. However, the optimization of the photografting needs more experiments in order to enable the incorporation of a broad range of surface chemistry at specific defined locations on the monolith. Indeed, the obtained retention factors are in line with those of a classic thermal grafting.

Laboratory of Analytical Sciences L.S.A.
U.M.R. 5180
43, Bd du 11 Novembre 1918
69622 Villeurbanne