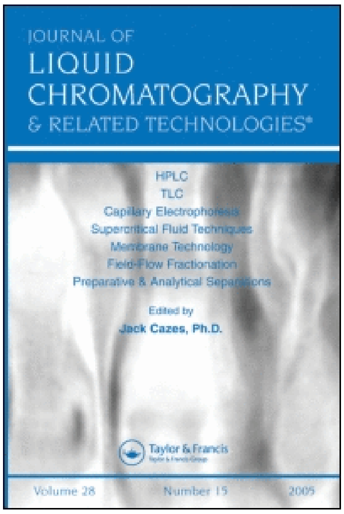

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# SURFACE MODIFICATION OF SILICA-BASED MONOLITH WITH POLY(PENTAFLUOROPROPYL METHACRYLATE) USING SINGLE STEP PHOTOGRAFTING

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# SURFACE MODIFICATION OF SILICA-BASED MONOLITH WITH POLY(PENTAFLUOROPROPYL METHACRYLATE) USING SINGLE STEP PHOTOGRAFTING

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☐ *Photografting has been utilized to achieve on-column functionalization of porous silica monoliths in capillaries. The pore surface was first modified with 3-((trimethoxysilyl)propyl) methacrylate ($\gamma$-MAPS) and then photografted in a single step with poly(pentafluoropropyl methacrylate) (PFM). The chromatographic performance of these grafted capillary columns was evaluated using reversed-phase separation of alkylbenzenes.*

**Keywords** alkylbenzenes, capillary column, monolith, pentafluoropropyl methacrylate, photografting, silica

## INTRODUCTION

Currently available inorganic silica-based monoliths are valued for their good mechanical stability and well defined porous properties.[1–5] However, the limited availability of silanization reagents enabling its pore surface modifications reduces the number of possible applications. To overcome this shortcoming, Ikegami et al.[6,7] introduced a thermally initiated polymerization of monomers with anion- and cation-exchange functionalities on the surface of a silica monolith modified with 3-methacryloxypropyltriethoxysilane. This approach eliminated the need for preparation of new silanization reagents, allowed "grafting to" polymerization, and provided a mixed-mode column, which exhibited both anion and cation exchange properties. A similiar procedure was utilized for preparation of highly retentive capillary columns for reversed-phase liquid chromatography.[8,9]

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In contrast to thermally initiated grafting, photografting benefits from the commercial availability of monomers with a wide variety of functionalities and can consequently expand the range of separation modes of silica-based monolithic columns. Rohr et al.[10,11] reported UV initiated radical polymerization as a method for control of surface chemistry of polymer monoliths located inside a fused silica capillary. The described grafting process anticipated formation of grafted chains that are further branched or crosslinked. The extent of grafting of the polymer chains was affected by the dose of UV light, which is a product of irradiation time and light intensity and by concentration of both photoinitiator and monomer in the reaction mixture. Ultimately, photografting was broadly adopted as an approach facilitating surface modification of porous polymer monoliths.[12–17] For example, Stachowiak et al.[16,17] utilized single step and sequential two step photografting for the preparation of porous polymer monoliths with desired surface chemistries. The single-step photografting approach involved irradiation of the monolith whose pores were filled with a solution of functionalized monomer containing a photoinitiator. The advantage of this approach is its simplicity. However, difficulty with dissolution of both monomer and initiator in a suitable solvent as well as the formation of significant amounts of nongrafted polymer in the solution that may clog the pores are the limitations. As an alternative, sequential two-step photografting was developed. This process requires first the grafting of the photoinitiator on the pore surface followed by filling the pores with a monomer solution and then, by reacting by graft polymerization. This approach enables dissolution of initiator and monomers in different solvents and provides polymerization in solution. This affords better surface coverage than the single-step photografting technique.

The objective of this communication is to introduce photografting as a novel method for fast and highly efficient on-column alteration of the surface chemistry of silica-based monolithic capillaries.

## EXPERIMENTAL

### Materials and Reagents

Urea, thiourea, uracil, ethylbenzene, benzophenone (BP), 2,2,3,3,3-pentafluoropropylmethacrylate (PFM), poly(ethylene) glycol (MW 10000, PEG), 3-((trimethoxysilyl)propyl) methacrylate ($\gamma$-MAPS) together with high purity solvents such as methanol, acetonitrile, and toluene were purchased from Sigma-Aldrich (St. Louis, MO). Tetramethyl orthosilicate (TMOS) and alkylbenzenes were purchased from Fluka (Buchs, Switzerland). DI water was obtained from an Easypure II LF Ultrapure water system from Barnstead International (Dubuque, Iowa). All other reagents used were of the highest purity and used as received. UV transparent Teflon-coated fused silica capillary (100 µm ID) was obtained from Polymicro Technologies (Phoenix, AZ).

## Instrumentation

Syringe pump KDS 210 from KD Scientific Inc (Holliston, MA) was used to pump solutions through capillaries. A Nikon Eclipse TE200 microscope (Melville, NY) provided monolithic evaluations from capillaries in each step of the process. A Micropublisher 5.0 CCD camera from QImaging (Burnaby, Canada) was used for the acquisition of images. Physical characterization of the monoliths—porosity, attachment to capillary walls and internal structure was accomplished by scanning electron microscopy (Topcon, Japan). An Oriel deep-UV illumination system series 8700 (Stratford, CT) fitted with a 500 W HgXe lamp was used for the UV exposure. The illumination controller used was a 2110C2 model from Radiation Power Systems (San Jose, CA) whose maximum wavelength was set at 254 nm. The irradiation power was calibrated to 11.9 mW/cm$^2$, using an OAI model 306 UV power meter with a 260 nm probe head. Chromatographic experiments were performed with an Agilent Technologies 1200 series solvent delivery system (Santa Clara, CA), which was equipped with a Rheodyne manual injector (Park Court, CA) and a Linear UVIS-205 absorbance detector (San Jose, CA).

## Activation of Capillaries

Prior the synthesis of silica monoliths, the inner surface of fused-silica capillary was activated by introducing an etching step.[18] Capillary was rinsed with 1 mol/L aqeous sodium hydroxide (NaOH), plugged with rubber septa, and placed in the oven for 3 hr at 120°C. After that, the capillary was rinsed with water and acetone for $\frac{1}{2}$ hr. Finally, capillary was dried with stream of nitrogen for 10 min and dried in the oven at 120°C for 1 hr.

## Preparation of Silica Monolith

Silica monoliths were prepared inside fused-silica capillary by a previously reported method.[22] The silica alkoxide, tetramethoxysilane (TMOS; 4 mL) was added to the solution of poly(ethylene) glycol (PEG, 1.24 g; MW = 10,000), urea (0.9 g) and acetic acid (0.01 mol/L, 10 mL) and vigorously stirred at 0°C for 45 min. The homogeneous mixture was then filtered through a 0.45 µm PTFE filter and charged into a pretreated capillary by nitrogen pressure and allowed to polymerize and age in the oven at 30°C overnight. The capillary was further kept in the oven for hydrothermal aging (gradient 30°C to 120°C in 15 hr at a rate of 0.1°C/min and hold for 3 hr at 120°C). The monolithic gel was further rinsed with water for 2 hr at a flow of 0.5 μL/min, and dried with nitrogen for two hr. The capillary was further subjected to surface modification.

### Surface Modification with Polymethacrylate

Prior the γ-MAPS attachment the silanol groups on the surface of porous silica monolith was activated by introducing an etching step. Capillaries were rinsed with 0.2 mol/L aqueous NaOH for 30 min, followed by 0.2 mol/L HCl for 30 min at a flow rate of 0.5 μL/min. Furthermore, capillaries were rinsed with water and acetone for 30 min and dried by nitrogen flushing for 1 hr. Then, a silanization mixture containing 10% v/v of γ-MAPS in toluene was charged in the capillary, which was plugged with rubber stoppers and allowed reaction at RT for 2 hr.[18] The capillary was then flushed with toluene at flow rate of 1 μL/min for 30 min, and further dried with nitrogen for 30 min.

### Single-Step Photografting

The attached methacrylate undergoes further polymerization with 2,2,3,3,3-pentafluoropropyl methacrylate (PFM) via UV initiated (254 nm) radical polymerization in the presence of benzophenone. A solution of 5 wt% of deaerated benzophenone in PFM monomer was pumped through the capillary for 30 min at a flow rate of 0.5 μL/min. The capillary was irradiated with UV light for indicated amount of time. The monolith was further rinsed with methanol for 60 min in order to remove any excess of reagent.

## RESULTS AND DISCUSSION

Silica monoliths were prepared inside a UV transparent capillary based on a previously reported procedure. The silanol groups on the monolith surface were activated by introducing an etching step, which was followed by an on-column reaction with γ-MAPS. The monolithic surface was further exposed to UV to initiate polymerization of pentafluoropropyl methacrylate using benzophenone[19–21] as radical initiator (Figure 1). Optimization of photografting conditions, such as adjustment of irradiation time and implementation of single or sequential two-step photografting, allowed for preparation of capillaries with varying chromatographic properties.

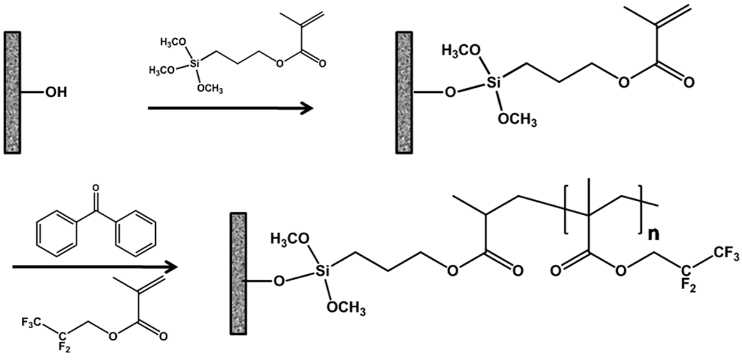


**FIGURE 1** Scheme of single step photografting procedure.

Chromatographic evaluation of photografted capillaries via the separation of alkylbenzenes enables monitoring of the grafting efficiency. Our preliminary comparison of the separation ability of capillaries prepared utilizing sequential two-step photografting versus single-step photografting have not revealed significant diferences in resolution. As a result, the more convenient single step photografting technique was used in the following experiments.

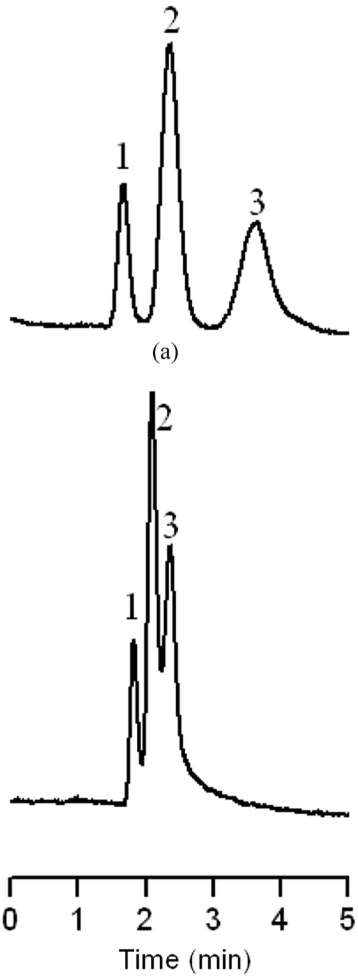
The duration of irradiation time determines the density of grafted functional groups on the monolith pore surface and this, subsequently, affects the performance of photografted capillaries. The qualitative effect of the duration of grafting time on the grafting efficiency and successive separation ability is shown in Figure 2. The improvement in column performance with increasing irradiation time can be attributed to higher extent of grafting that projects to better surface coverage with fluorinated functionalities.

Complete separation of selected alkylbenzenes shown in Figure 3 was achieved with a column grafted for 5 min. The elution order in the chromatogram confirms the effect of polarity of analytes that are separated according to the strength of their hydrophobic interaction with the stationary phase and indicates reversed-phase separation mechanism.

The hydrophobicity of the alkylsilica-bonded phase is commonly characterized by measuring relative retention of homologous series of n-alkylbenzenes[22,23] and expressed as the methylene selectivity, $\alpha$. This value is calculated from the slope of logarithm of retention factor $k$ plotted against the number of carbon atoms in alkyl chain of n-alkylbenzenes $n_c$ using Equation (1).[24]

$$\log k = \mathrm{n_c} \log \alpha + \log \beta \qquad (1)$$

Using retention factors from chromatogram shown in Figure 3, we created plot presented in Figure 4 and calculated the methylene selectivity $\alpha = 2.08$ for the modified monolith with 20% aqueous acetonitrile mobile phase.



(a)

(b)

**FIGURE 2** Chromatographic separation of alkylbenzene using silica-based monolithic capillary with anchored γ-MAPS and photografted PFM. Conditions: capillary 25 cm × 100 μm I.D., 0.5 min (a) and 5 min (b) single step photografting; mobile phase 40% aqueous acetonitrile; flow rate 1 μL/min; detection wavelength 214 nm. Peaks: thiourea (1), propylbenzene (2), and hexylbenzene (3).

Moravcova et al.[25] reported $\alpha = 1.54$ in 70% aqueous acetonitrile for commercial monolithic silica capillary column Chromolith CapRod with C18 functionality. The higher value of methylene selectivity observed for our capillary indicated significantly higher hydrophobicity of fluorinated functionalities compared to that of octadecyl ligands. It is worth noting that the separation was achieved using an environmentally friendly mobile phase containing much less organic modifier, acetonitrile.

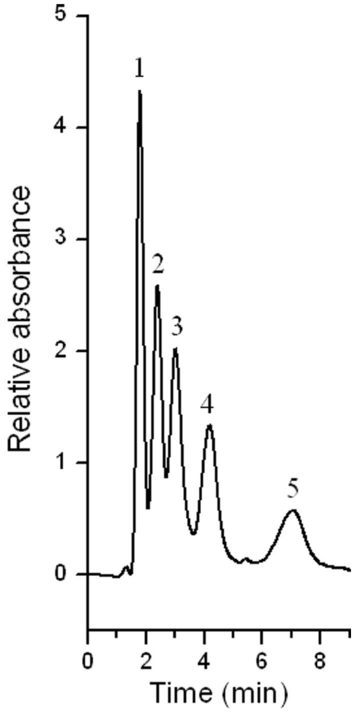


**FIGURE 3** Chromatographic separation of alkylbenzene using silica-based monolithic capillary with anchored γ-MAPS and photografted PFM. Conditions: capillary 21.8 cm × 100 μm I.D., 5 min single step photografting; mobile phase 20% aqueous acetonitrile; flow rate 1 μL/min; detection wavelength 254 nm. Peaks: uracil (1), benzene (2), methylbenzene (3), ethylbenzene (4), and propylbenzene (5).

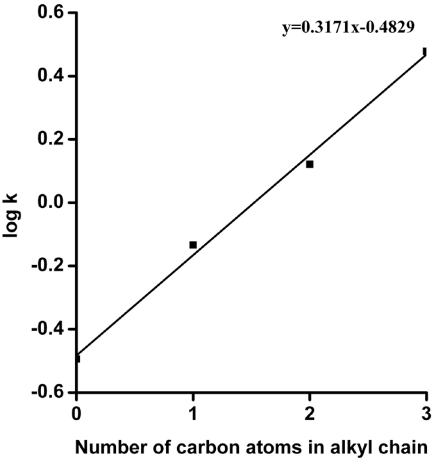


**FIGURE 4** Logarithm of retention factor (log k) versus the number of carbon atoms in alkyl chain of n-alkylbenzene.

## CONCLUSIONS

Our novel photografting process demonstrated here, which utilized a single fluorinated monomer as a model, can readily be extended to many other UV transparent monomers, thus, benefiting from the commercial availability of monomers with various functionalities. As a consequence, preparation of monolithic silica-based separation media with a wide variety of surface chemistries suitable for the separation in different chromatographic modes is possible. Our current research focuses on an increase in column efficiency via improving mass transfer characteristics. One of the avenues we test is control of pore size distribution and optimization of irradiation conditions.

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