



## Photografted fluoropolymers as novel chromatographic supports for polymeric monolithic stationary phases

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### ARTICLE INFO

#### Keywords:

Photografting  
Fluoropolymer  
Ethylene-tetrafluoroethylene  
Monolithic column  
Reversed-phase liquid chromatography

### ABSTRACT

In this study, porous polymer monoliths were in situ synthesized in fluoropolymers tubing to prepare microbore HPLC columns. To ensure the formation of robust homogeneous polymer monoliths in these housing supports, the inner surface of fluoropolymer tubing was modified in a two-step photografting process. Raman spectroscopy and scanning electron microscopy (SEM) confirmed the successful modification of the inner poly(ethylene-co-tetrafluoroethylene) (ETFE) wall and the subsequent attachment of a monolith onto the wall. Poly(glycidyl methacrylate-co-divinylbenzene), poly(butyl methacrylate-co-ethylene glycol dimethacrylate) and poly(styrene-co-divinylbenzene) monoliths were in situ synthesized by thermal polymerization within the confines of surface vinylized ETFE tubes. The resulting monoliths exhibited good permeability and mechanical stability (pressure resistance up to 9 MPa). The chromatographic performance of these different monolithic columns was evaluated via the separation of alkyl benzenes and proteins in a conventional HPLC system.

### 1. Introduction

Porous polymer-based monoliths have attracted substantial interest in the last years and have been satisfactorily applied as chromatographic supports in the field of bio-separation [1,2]. It is worth noting that most of these works reported until now have used fused-silica capillaries (75–200  $\mu\text{m}$ ) as common supports for the preparation of these monolithic columns due to the simplicity of the covalent bonding of the monolith onto the modified inner wall via previous vinylization of the silica surface. However, capillaries are hardly adaptable to conventional HPLC systems, since they require working at very low flow rates, small injection volumes, minimal extra-column and detector cell volumes, which increased the cost of the analytical instrumentation (capillary/nano-LC).

In the last years, few efforts have been made to fabricate microbore monolithic columns (0.5–1.0 mm i.d.) using different housing materials such as glass [3], silicosteel [4], titanium [5], polyether ether ketone (PEEK) [6,7], or polypropylene (PP) tubing [8]. Although these approaches have obtained varying degrees of success, the columns may suffer from the shrinkage of the monolith due to the upscaling process. For instance, the monolith shrinkage during polymerization, albeit negligible in capillaries, it is strong enough to breakdown the monolith-

tube anchorage when larger diameter tubes are employed. In this sense, certain strategies have been proposed, such as the use of an external mold together with a proper selection of monomers providing a highly flexible polymer [9], a titanium scaffold [10], solvents that keep the stationary phase in the swollen-state [11], and polymerization under high pressures [12].

Fluoropolymers represent a rather specialized group of polymeric materials with large number of new types being continuously developed. Some are derivatives of the original polytetrafluoroethylene (PTFE), such as fluorinated ethylene propylene, perfluoroalkoxy copolymers and ethylene-co-tetrafluoroethylene (ETFE) [13]. These materials are known to have excellent chemical resistance, good mechanical properties, high thermal stability, low dielectric constant and transparency to UV radiation [13]. These polymers have been used in numerous industrial applications, such as in aerospace, automotive, petrochemicals, medical, microelectronics and electrical industries [13]. Also, they have been used as suitable materials in analytical field including sample preparation and optical devices, automation methods, trace metal analysis, etc. Their favorable properties, together with the fact that they can be easily and cheaply purchased in different formats and sizes, make fluoropolymers a good choice as housing material in the preparation of monolithic polymer columns, either with preparative

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or analytical purposes. However, the hydrophobicity and low reactivity of fluoropolymers have hindered the onset of stationary phases covalently attach to fluoropolymer surfaces until very recently.

Surface modification of fluoropolymers has been reported by means of several wet chemical treatments [9,14–16], as well as by some physical procedures such as plasma [17], ion beam [18],  $\gamma$ -radiation [19], extreme UV light [20] or vacuum UV light [21]. However, the physical treatments cannot be easily used to modify the inner surface of narrow tubes, since they are not routinely available in most laboratories, and moreover they can produce the degradation of the fluoropolymers [16]. Among the chemical treatments, the use of etchant reagents such as sodium naphthalene solution (Fluoroetch<sup>®</sup>) [22,23], peroxide/sulfuric acid [24] or permanganate/nitric acid mixtures [25] have been proposed to introduce polar groups such as hydroxyls or carboxylates onto fluoropolymer surfaces.

Recently, we have described the preparation of methacrylate-based monoliths in PTFE tubing using a surface modification method similar to those described in ref. [9]; however environmental and safety concerns as well as the difficulties in controlling the depth profiles of the treatments make these methods unsuitable from a green and sustainable perspective.

An alternative strategy for polymer surface modification and functionalization involves the use of UV photografting technology, which represents simple and clean technique [26]. In addition, this technology is characterized by low electrical power input and energy requirements, low temperature operation and no volatile compounds release. It has been used to modify the surface of different polymers (polyolefins, polyesters, polyamides and polyethers) [27,28] and, particularly, PP-based materials in several formats, such as pipette tip [29,30] or tubes [8,31] for anchoring polymer monoliths. This process can be described as follows. Firstly, radicals are formed onto the polymeric surface through a photo-reduction reaction between a photoinitiator (commonly benzophenone, BP) and the C–H bonds. Then, the new generated radical initiates the polymerization of the monomers (added together with the photo-initiator or in a following step), resulting in graft polymer chains chemically bonded onto the substrates [27]. Due to the higher difficulty that defluorination entails, BP in combination with strong reducing agents (e.g. sodium hydride) has been described for surface modification of PTFE or other fluoropolymers [23]. Also, other photosensitizers such as xanthone have been described for the surface modification of PTFE or ETFE materials [16].

The goal of this study was to develop a monolithic column for its use in microbore HPLC using a photografted fluoropolymer tubing as housing material. For this purpose, several fluoropolymer tubes (0.75–0.8 mm i.d.) were treated with a two-step UV photografting process to make possible the anchorage of monolith to fluoropolymer wall. Using ETFE as probe material, the grafting conditions were optimized in order to provide a robust covalent anchorage of the monolith to the fluoropolymer surface. To our knowledge, this modification technique has not been explored yet in fluoropolymer materials to host polymer monoliths as stationary phases. Three different polymers based on glycidyl methacrylate, butyl methacrylate and styrene monomers, were prepared in ETFE tubing using the optimized photografting treatment, and they were applied to the separation of alkylbenzenes and proteins in a conventional HPLC system. As far as we know, this is the first time that photografted ETFE tubes were used as housing material for polymer monoliths and its use in reversed-phase LC separation.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Glycidyl methacrylate (GMA), butyl methacrylate (BMA), ethylene glycol dimethacrylate (EDMA), tetrahydrofuran (THF), 1,4-butane-diol, 1-propanol and trifluoroacetic acid (TFA) were from Sigma-

Aldrich (Steinheim, Germany). Styrene (STY), divinylbenzene (DVB) (technical grade, 80% mixture of isomers, 20% mainly ethylstyrene), 1-decanol, 1-dodecanol, benzophenone (BP) and lauroyl peroxide (LPO) were supplied by Alfa Aesar (Karlsruhe, Germany). Azobisisobutyronitrile (AIBN) was from Fluka (Buchs, Switzerland). HPLC-grade acetonitrile (ACN) and methanol (MeOH) were from Merck (Darmstadt, Germany). Uracil, alkyl benzenes from Riedel de Haën (Seelze, Germany) and proteins such as ribonuclease A (bovine heart), cytochrome C (bovine pancreas) from Alfa Aesar, and myoglobin (horse skeletal muscle) from Sigma were used as probes. Acetone was supplied by Panreac (Barcelona, Spain). Ultra-pure water was obtained with a Puranity TU6 water purification system from VWR (Bedford, MA, USA) provided with a 0.2  $\mu\text{m}$  filter. Unless otherwise stated, any other chemicals used were of analytical grade. PTFE tubing of 1/16" (1.6 mm) o.d.  $\times$  0.8 mm i.d. from Omnifit (Fisher Scientific, Loughborough, UK), fluorinated ethylene propylene (FEP), perfluoroalkoxy (PFA) and ETFE tubing of 1/16" (1.6 mm) o.d.  $\times$  0.75 mm i.d. from Vici Jour (Schenkon, Switzerland) were also used. ETFE tubing of 1/8" (3.2 mm) o.d.  $\times$  1.57 mm i.d. from IDEX Health & Science LLC (Washington, USA). The chemical structures of the fluoropolymers investigated are given in Fig. 1.

Stock solutions of alkyl benzenes were prepared in ACN at 1.0 mg mL<sup>-1</sup> each and kept at 4 °C until their use. Working standard solutions were freshly prepared by dilution to the desired concentration with the mobile phase. Proteins were dissolved in water at concentration of 1.0 mg mL<sup>-1</sup> each and kept at -18 °C.

### 2.2. Instrumentation

An UV crosslinker (model CL1000) from UVP (Upland, CA, USA) equipped with UV lamps (5  $\times$  8 W, 254 nm) was used for photografting of fluoropolymer tubings. A syringe pump (Model 100, KD Scientific, New Hope, PA, USA) was employed to introduce the reagents into the supports. SEM photographs of fluoropolymer surfaces and monolithic materials were performed with a scanning electron microscope (S-4800, Hitachi, Ibaraki, Japan) provided with a field emission gun, and an EMIP 3.0 image data acquisition system. Previous to the SEM measurements, the polymeric sorbents were sputter-coated with Au/Pd for 2 min to avoid charging problems. Raman spectra of fluoropolymer surfaces were recorded with an XploRA One Raman microscope (Horiba Scientific, Villeneuve d'Ascq, France) from 150 to 3500 cm<sup>-1</sup> using 532 nm as excitation wavelength with a laser power of 90  $\mu\text{W}$ .

Chromatographic analysis was carried out in an HPLC equipment

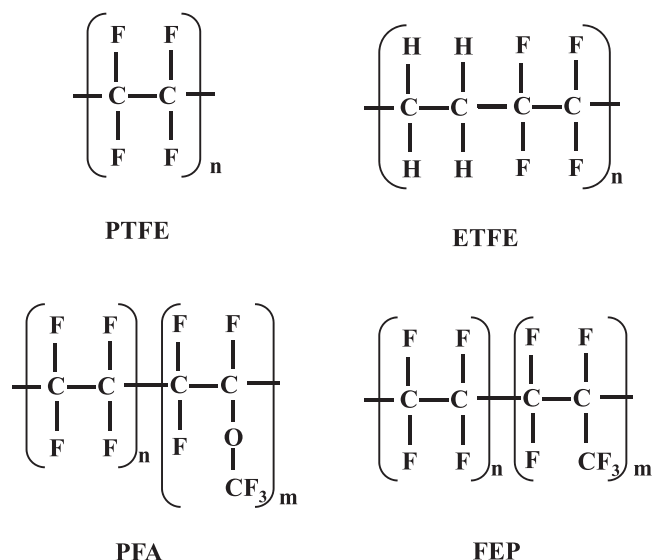


Fig. 1. Structures of fluoropolymers investigated in this study.

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