Polymer 51 (2010) 5890–5894

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymer Communication

Porous polystyrene-based monolithic materials templated by semi-interpenetrating polymer networks for capillary electrochromatography

Thanh-Xuan Lav, Benjamin Carbonnier, Mohamed Guerrouache, Daniel Grande*

Institut de Chimie et des Matériaux Paris-Est, UMR 7182 CNRS – Université Paris-Est Créteil Val-de-Marne, 2, rue Henri Dunant, 94320 Thiais, France

ARTICLE INFO

Article history:
Received 22 July 2010
Received in revised form
6 October 2010
Accepted 16 October 2010
Available online 8 November 2010

Keywords:
Porous polymeric monoliths
Semi-interpenetrating polymer networks (semi-IPNs)
Capillary electrochromatography (CEC)

ABSTRACT

Porous polystyrene-based monolithic columns were engineered through the *in-situ* generation of poly(ε-caprolactone) (PCL)/polystyrene (PS) semi-interpenetrating polymer networks (semi-IPNs), followed by the extraction of the uncrosslinked partner acting as a polymeric porogen. In a first stage, the semi-IPNs were prepared within the confines of fused silica capillaries by UV-initiated free-radical copolymerization of styrene and divinylbenzene, in the presence of PCL oligomers. In a second stage, the quantitative extraction of uncrosslinked oligoesters led to the formation of porous frameworks with a hierarchical porosity, as evidenced by SEM and DSC-based thermoporometry. Such as-obtained porous monoliths could be efficiently used as reversed-phase stationary phases for the separation of alkyl benzene derivatives by capillary electrochromatography (CEC).

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1. Introduction

Porous polymeric materials have attracted much interest as they find a wide array of applications in many areas, including separation and filtration techniques, biomolecule immobilization, controlled drug release, supported catalysis as well as template-assisted synthesis of nanomaterials [1]. Considering the synthesis of porous polymer monoliths, a large variety of preparation methods has been reported so far, such as classical free-radical polymerization processes with thermal or UV initiation, polymerizations using high energy radiations (γ-rays, electron beam irradiation), controlled/living polymerizations and polycondensation reactions [2–6]. In this regard, Svec has recently published an excellent review on the different techniques for engineering such materials with well-controlled pore and surface chemistry characteristics [7].

The basic idea associated with the design of porous polymers underlies the introduction of a porogenic agent (*i.e.* solvent, gas, small molecule or macromolecule) within polymer structures, followed by its selective removal. Both the nature and the amount of a pore-forming solvent are key features for controlling the porous properties of the resulting monolithic materials through the solvation of growing polymer chains during the polymerization process. The most widely used approach relies on the combination of a macroporogen (thermodynamically poorer solvent acting in the early stages of the phase separation process) with a microporogen (good solvating porogenic solvent). The choice of a porogen pair remains largely empirical rather than based on predicted considerations. This is the reason why the number of applied porogens is still limited, and proven porogen mixtures are mostly applied to miscellaneous chemically different polymer systems. Alternatively, semi-interpenetrating polymer networks (semi-IPNs), *i.e.* macromolecular assemblies constituted of a methacrylic sub-network and an entrapped linear polymer acting as a polymeric porogen, have been proposed as precursors for the design of porous polymeric monoliths [8]. The synthetic strategy of semi-IPNs generally implies that, starting from homogeneous reactive solutions, biphasic polymeric structures are obtained, as the polymerization and cross-linking of co-monomers is performed in the presence of an uncrosslinked polymer. Among the parameters controlling the spatial scale of phase separation, in other words the factors tuning the porous structure in terms of pore sizes and pore size distributions, the polymer–polymer miscibility plays a dominant role. On the other hand, as far as poly(styrene-*co*-divinylbenzene) porous materials are concerned, (i) a sole porogenic solvent, including tetrahydrofuran, acetonitrile, toluene, chlorobenzene, hexane, and methanol, (ii) mixtures of toluene with high molar mass alcohols, as well as (iii) oligomers have been used to generate permanent porous structures [9–13].

Our group has recently reported a straightforward and versatile approach for engineering (nano)porous networks with tunable porosity [14]. Such porous materials are templated by oligoester-containing semi-IPNs, and can be readily derived through the

* Corresponding author. Tel.: +33 1 49 78 11 77; fax: +33 1 49 78 12 08.
E-mail address: grande@icmpe.cnrs.fr (D. Grande).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.10.032

extraction of uncrosslinked oligomers embedded in a vinylic subnetwork. Herein, we propose to extend the semi-IPN approach to the preparation of highly cross-linked porous polymer monoliths directly within the confines of fused silica capillaries. Porous networks derived from poly(ε-caprolactone) (PCL)/polystyrene (PS) semi-IPNs are synthesized by UV-initiated copolymerization of the corresponding monomer and divinylbenzene, in the presence of a PCL oligomer as a porogen template, followed by the quantitative PCL extraction. The resulting monoliths are characterized by complementary physico-chemical techniques. A structural characterization is performed *in-situ* by Raman spectroscopy, after the photopolymerization and extraction steps. The occurrence of organizational features in the porous structure of PS-based monoliths is demonstrated by scanning electron microscopy (SEM), mercury intrusion porosimetry (macroporosity) and DSC-based thermoporometry (mesoporosity). The baseline separation of alkyl benzene derivatives demonstrates the analytical potentialities afforded by these monolithic columns as reversed-phase stationary phases for capillary electrochromatography (CEC) applications.

2. Experimental

2.1. Materials

Dihydroxy-telechelic PCL oligomers (M_n = 530 g mol^{-1}, M_w/M_n = 1.2) and sodium phosphate monobasic monohydrate (NaH_2PO_4,H_2O) were purchased from Aldrich and used without further purification. 2,2′-azobisisobutyronitrile (AIBN, Merck) was purified by recrystallization from methanol. Styrene (S) and divinylbenzene (DVB, technical grade 80%) were purchased from Aldrich and distilled under vacuum prior to use. 3-(trimethoxysilyl)propyl methacrylate, sodium hydroxide (NaOH), hydrochloric acid (HCl), alkyl benzenes (with side chain size ranging from methyl to *n*-hexyl group), and sodium phosphate dibasic dodecahydrate (Na_2HPO_4,12H_2O) were purchased from Fluka. Toluene was obtained from Carlo Erba. HPLC-grade acetonitrile (ACN), *N*,*N*-dimethylformamide (DMF) was obtained from Sigma. HPLC-grade tetrahydrofuran (THF) was purchased from Prolabo. All these reagents were used without further purification. Phosphate buffers (PBS) (NaH_2PO_4,H_2O and Na_2HPO_4,12H_2O) were prepared in deionized water, adjusted to the desired pH value, and filtered with Buchner. Hydro-organic mobile phases were prepared by mixing the appropriate amount of acetonitrile with the phosphate buffer (5 mmol L^{-1}, pH 6.8).

2.2. Preparation of monolithic capillaries

Fused silica capillaries with a UV-transparent external coating (75 μm I.D. × 325 μm O.D.) were obtained from InnovaQuartz. Prior to the polymerization, their inner walls were pretreated in order to ensure the stability of the monolithic columns. This pretreatment consisted of a vinylization step using 3-(trimethoxysilyl)propyl methacrylate as a bifunctional reagent [15]. The monolithic capillaries were obtained by the *in-situ* preparation of PCL/PS semi-IPNs, followed by the PCL extraction (Fig. 1).

In a typical experiment, 0.167 g of PCL as the linear porogenic oligomer (40 wt.%), 0.155 g (1.49 mmol, 37 wt.%) of styrene, and 0.095 g (0.73 mmol, 23 wt.%) of DVB were homogeneously mixed in a flask, before adding AIBN (9.7 mg, 0.059 mmol, $[AIBN]_0/([S]_0 + 2[DVB]_0) = 0.02$). The pretreated capillary was filled with a large excess of this mixture, then sealed with rubber septa, and irradiated at 365 nm for 15 min. For this purpose, a Spectrolinker XL-1500 UV crosslinker oven (Spectronics) fitted with six 15 W lamps was used. After the polymerization was completed, the monolithic capillary was washed with THF with a flow rate of

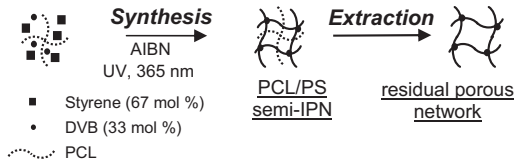

Fig. 1. Design of porous polystyrene-based networks from PCL/PS semi-IPNs.

1 μL min^{-1} under an applied pressure of about 30 bar for 30 min to remove the PCL oligomers.

The capillary was then cut at both ends to a total length of 30.3 cm. In order to create a detection window for chromatographic analyses, a small part of the capillary (0.8 mm) was irradiated overnight with the UV detection system of a capillary electrophoresis (CE) apparatus under flow in the presence of the eluent used subsequently (mixture of 70 vol.% acetonitrile and 30 vol.% phosphate buffer). Under these conditions, no significant removal of the capillary coating was observed.

2.3. Instrumentation

SEM analyses were performed with a LEO 1530 microscope equipped with a high-vacuum (10^{-10} mmHg) Gemini column. The accelerating tension was 1 kV. Microscopic observations were performed for polymer samples within the capillaries as-obtained, after polymerization and after extraction with THF. Prior to analyses, the capillaries were cut at different places, and small pieces were deposited on a SEM support with a silver-containing solution. The samples were then dried under vacuum, and coated with a platinum/palladium alloy (5 nm) in a Cressington 208 HR sputter-coater.

Mercury intrusion porosimetry analyses were performed using a Micromeritics AutoPore IV 9500 porosimeter.

Thermoporometry analyses were performed by Differential Scanning Calorimetry (DSC) with a TA Instruments 2010 calorimeter, using water as the penetrant solvent. The scans were run from − 50 to 5 °C at a heating rate of 1 °C min^{-1}. The experimental procedure and the equations applied for the determination of the pore size distribution profiles were detailed in previous reports [16].

The chemical structure of the monoliths was investigated using a Raman spectrometer LabRAM HR from Horiba Jobin Yvon equipped with a laser emitting at 633 nm. The acquisition time was fixed at 1 min.

All the electrochromatographic experiments were performed on a P/ACE MDQ model CE apparatus equipped with a 32 Karat software (version 5.0) for data acquisition.

3. Results and discussion

3.1. Preparation and structural characterization of porous monoliths

Porous polymeric monoliths were engineered through the *in-situ* generation of PCL/PS semi-IPNs in capillary columns at room temperature, followed by the THF extraction of liquid PCL oligomers under pressure. The chemical nature of both partners in semi-IPNs was purposely selected as a function of their solubility parameters [17]. As a matter of fact, the use of incompatible polymers, such as PCL and PS, along with a fast polymerization rate for the S/DVB cross-linking reaction, is expected to lead to an early phase separation process and a high extent of final phase separation, thus facilitating the removal of the PCL uncrosslinked partner within the confines of capillaries. This is a prerequisite to design highly permeable polymer monoliths with flow-through pores and advanced chromatographic properties. For the free-radical

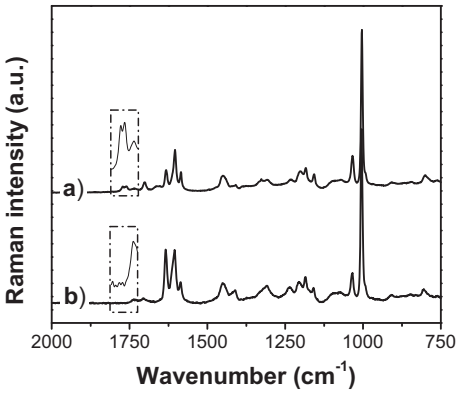

Fig. 2. Raman spectra recorded for PCL/PS semi-IPNs as-obtained: (a) before, and (b) after PCL extraction.

polymerization reaction, a photo-initiation process upon UV irradiation at 365 nm was selected because at this wavelength both styrene and divinylbenzene are transparent, so that the decomposition rate of AIBN might not be influenced by the aromatic comonomers. Directly after the rapid photopolymerization process, filling homogeneity along the whole capillary was checked by evaluating the transparency of the monolithic capillary column through optical microscopy.

To confirm the quantitative extraction of PCL, the semi-IPNs within the capillaries were directly analyzed by Raman spectroscopy. Fig. 2 shows typical Raman spectra for the as-obtained polymeric materials before (Fig. 2 a) and after (Fig. 2 b) the extraction step. The bands at 1632, 1603 and 1585 cm^{-1} corresponding to the aromatic derivatives are present on both spectra. In contrast, the band at 1757 cm^{-1} assigned to the carbonyl stretching vibration from the PCL ester groups disappeared after rinsing with THF. Interestingly, no unreacted vinylic groups could be detected before extraction, thus suggesting a completion of the S/DVB cross-linking process. The latter assertion was confirmed by a ^1H NMR analysis of the sol fraction derived from the extraction of the corresponding bulk semi-IPN: only initial PCL oligomer was recovered. These findings corroborated first the successful photo-initiated copolymerization of styrene and DVB along with a high cross-linking degree, and second, the quantitative removal of the linear oligoester from the PS-based matrix. As a consequence, the resulting porous structures should provide good flow-through properties to the monoliths.

3.2. Morphological characterization of porous monoliths

To gain further insight into the porosity of semi-IPN-derivatized monolithic materials, SEM observations were performed to probe their morphology. Before extraction, the polymeric materials displayed a compact and non porous structure (Fig. 3 a), while the corresponding network as-observed after PCL extraction revealed a highly porous framework whose pore sizes ranged from 100 nm to a few μm (Fig. 3 b and c). Such observations are in good agreement with the mercury intrusion porosimetry analysis performed on the corresponding bulk sample prepared under experimental conditions identical to those employed for the capillary columns: an average pore size around 500 nm was thus determined (data not shown). Moreover, a typical monolithic structure made of small globuli fused together into a single skeleton forming a rigid and yet permeable polymeric support with interconnected pores can be easily recognized from Fig. 3 b. The morphological data obtained from SEM allowed only for the investigation of macroporosity, whereas the DSC-based thermoporometry technique permitted to access to the pore size distribution profile in the mesopore range. The pore sizes could be estimated between 15 and 50 nm with a maximum at 30 nm (Fig. 3 d). Even though the volume of mesopores derived from the pore size distribution was very low (0.15 $cm^3\ g^{-1}$), their presence was also expressed by the existence of a non negligible specific surface area equal to about 20 $m^2\ g^{-1}$. The occurrence of such organizational features strongly suggested that the semi-IPN-derivatized monoliths possessed a hierarchically structured porosity with a vast majority of macropores and a minority of mesopores.

3.3. Electrochromatographic properties of porous monolithic capillaries

On the basis of the aforementioned data and inspired by the results recently reported on the generation of an electro-osmotic flow (EOF) on uncharged poly(styrene-*co*-divinylbenzene)-based monolithic capillary columns [18], the newly prepared monoliths under investigation were applied to the separation of aromatic compounds by CEC.

The mechanism of EOF generation in typical CE or CEC experiments is associated to the formation of an electric double layer resulting from the accumulation of counter-ions from the electrolyte in close vicinity of a charged solid surface. In the absence of surface charges, it is assumed that the adsorption of ions from the water-containing mobile phase is responsible for the occurrence of an EOF, thus enabling fluid transport through the interconnected pore structure of the monolith. One such phenomenon has been well described for polar and non-polar methacrylate-based monoliths by El Rassi's group [19]. For styrenic neutral monoliths, a similar effect was reported by Gusev et al.,[20], and an outstanding explanation based on molecular modeling was given by Buszewski [18]. The authors highlighted the crucial significance of the presence of water molecules in the mobile phase to allow for

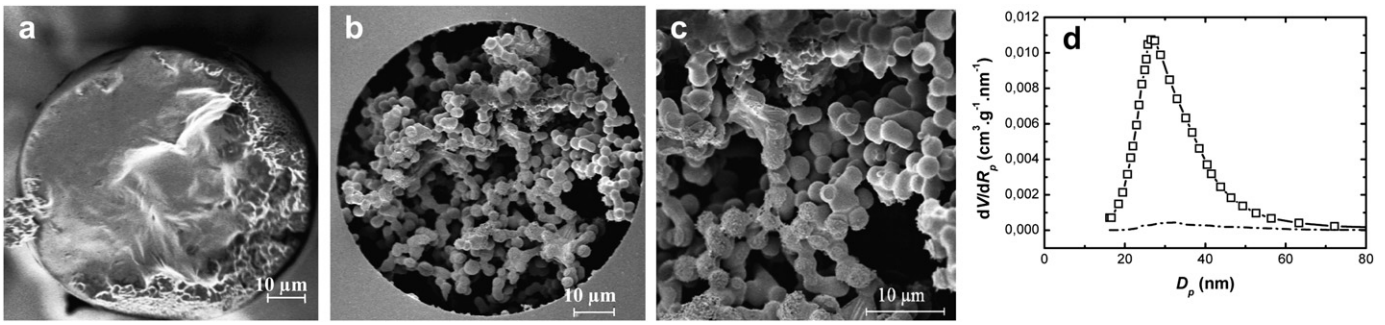

Fig. 3. SEM micrographs of cross sections associated with a PCL/PS semi-IPN monolithic capillary column: (a) before PCL extraction, (b) and (c) after PCL extraction. (d) Pore size distribution profiles as determined by DSC-based thermoporometry for corresponding bulk monoliths (-·- before PCL extraction, ▫ after PCL extraction).

ion adsorption on hydrophobic polystyrene-based surfaces. In this respect, the porous monoliths derived from PCL/PS semi-IPNs were initially conditioned with hydro-organic eluent under hydrodynamic flow, prior to evaluate their electro-osmotic properties using DMF as a neutral marker. A stable cathodic EOF equal to about 2.5×10^{-4} cm^2 V^{-1} s^{-1} was observed by applying a positive voltage and using a mobile phase containing a mixture of 70 vol.% ACN and 30 vol.% of 5 mmol L^{-1} phosphate buffer (pH 6.8), which resulted in an EOF velocity of 1.69 mm s^{-1} at a running voltage of 20 kV.

In reversed-phase electrochromatography, the migration of neutral compounds is based on the relative hydrophobicity of the analytes, and is mainly affected by the composition of the mobile phase. Accordingly, as the length of the aliphatic side chain of injected alkyl benzenes increased, the retention time increased, thus affording the baseline separation of six alkyl benzene derivatives within less than 8 min (Fig. 4). It should be stressed that faster separations could be achieved by Lubbad et al. through micro-HPLC in the presence of a composition gradient for the hydro-organic mobile phase [21]. The largest theoretical plate numbers of our monolithic columns could reach up to 100 000 plates m^{-1} for DMF and 70 000 plates m^{-1} for toluene (C_1). For the homologous alkyl benzene series under consideration, the plot of logarithmic retention factor (log k) versus the number of carbon atoms in the aliphatic substituent exhibited a linear dependence, as shown in the inset of Fig. 4. The methylene selectivity α_{CH_2} was determined from the slope value and was equal to 1.40. This calculated value was comparable to those reported for methacrylate-based monoliths bearing surface-grafted aliphatic side groups as reversed-phase selectors [22,23], which demonstrated the discrimination potential of the semi-IPN-derivatized styrenic monoliths. Moreover, the influence of varying the ACN content in the mobile phase (from 45 to 75 vol.%) on the retention of alkyl benzenes was also investigated (data not shown). It turned out that the retention time of each solute increased linearly as the content of the organic modifier in the eluent decreased. The whole set of results confirmed the reversed-phase electrochromatographic behavior of the monolithic capillary columns templated with PS-based semi-IPNs [24,25].

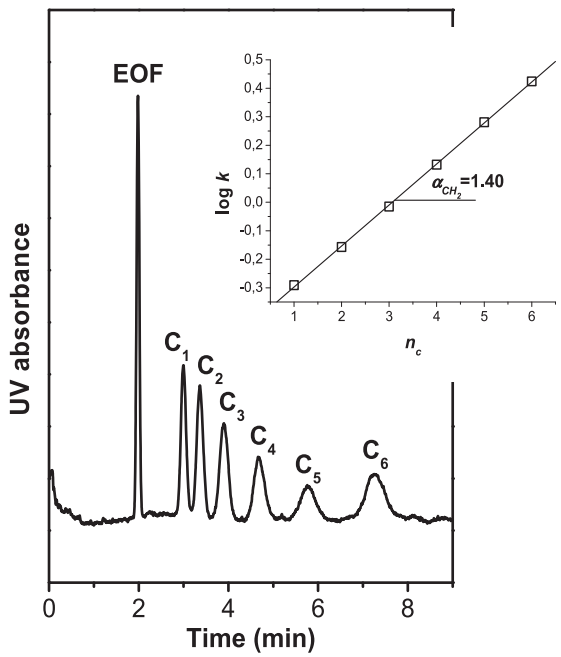

Fig. 4. Electrochromatographic separation of alkyl benzenes injected on polystyrene-based monolithic column. CEC conditions: mobile phase: ACN/PBS (5 mmol L^{-1}, pH 6.8) 70/30 vol.%; column length: 20 cm to detector, 30.3 cm overall; injections 10 kV for 10 s, running voltage 20 kV at 25 °C; UV detection at 214 nm. *Inset*: Plot of logarithmic retention factor (log k) vs. number of carbon atoms in the side chain (n_C) of injected alkyl benzene.

Lastly, it is noteworthy that monolithic column packing should be incompressible under the conditions used in CEC. As a simple test, occasional visual examination by optical microscopy did not show any gaps or other irregularities in the packing over three months of operation with a running voltage of 20 kV. To further check their mechanical stability, the monolithic columns were tested by pumping THF, acetonitrile, and water at inlet pressures up to 100 bar. The flow rate as a function of the pressure drop varied linearly (data not shown), suggesting that the packing was not compressed. Due to the highly cross-linked structure of our polystyrene-based monoliths, and the occurrence of large flow-through channels in such frameworks, the potential problems associated with swelling in THF and shrinkage in acetonitrile should be neglected in the electrochromatographic experiments. Besides good mechanical stability, a consequence of the low swelling propensity was the excellent run-to-run reproducibility in retention times that was checked by four injections of alkyl benzenes within one month (relative error lower than 2%).

4. Conclusions

This contribution has expanded the spectrum of porous frameworks that can be engineered through the use of semi-IPNs as nanostructured precursors. The extraction of uncrosslinked oligoesters from PCL/PS semi-IPNs does constitute a straightforward and effective strategy for generating macro- to meso-porous PS monoliths. Thus, uncrosslinked PCL sub-chains may well serve as porogen templates for the design of such porous polymer networks.

The *in-situ* formation of porous monolithic materials through the semi-IPN approach in capillary columns may represent an original and valuable alternative route to stationary phases for advanced chromatographic techniques. Such semi-IPN-templated monoliths indeed allowed for the efficient and rapid separation of alkyl benzene derivatives by CEC. Other aromatic families, such as phenol derivatives and polycyclic aromatic hydrocarbon compounds, could also be envisioned. The electrochromatographic data derived there from as well as the dependence of the chromatographic properties on the morphology associated with the monolithic stationary phases, in terms of pore size and porosity ratio, will be published in a forthcoming paper.

Acknowledgements

The authors thank the French Ministry of Research for providing T.-X. Lav with a post-doctoral grant. They are also indebted to Prof. M.-C. Millot (Université Paris-Est Créteil Val-de-Marne) for helpful discussions, as well as Dr. C. Paris (CNRS, Thiais) for her kind assistance in Raman spectroscopy.

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