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Original Paper

Visible light-induced photopolymerization of an *in situ* macroporous sol–gel monolith

A one-step, *in situ*, photopolymerization of a mixture of methacryloxypropyltrimethoxysilane in the presence of an acid catalyst, water, and toluene is accomplished in a 75 μm id polyimide-coated capillary using visible light (460 nm) for a 15 min irradiation time. The mixture is a two-component photosystem comprising Irgacure 784 photosensitizer and diphenyliodonium chloride photoinitiator. The visible photopolymerized sol–gel (vis-PSG) column shows RP chromatographic behavior. The analytical potential of these columns is demonstrated with the isocratic separation of small, neutral alkyl phenyl ketones. Operational parameters, such as mobile phase composition, field strength, and column temperature were varied to assess how they affect the separation performance of the monolith.

Keywords: Capillary electrochromatography / Cationic / Monolith / Photopolymerized / Visible

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1 Introduction

Polymer-based monolithic stationary phases have been developed over the past few decades as alternative column materials to the classical particle-packed column technology for CEC and LC. Monoliths are prepared by *in situ* thermal or photoinduced polymerization of a solution containing a monomer, an initiator, and a porogen inside column tubings. Both organic-based and organic–inorganic hybrid monoliths have been reported [1–7]. The ease with which these monoliths are prepared has allowed them to be successfully used in CEC.

We suggest that photopolymerizations that typically involve a free radical at the propagating active center offer significant advantages over the more conventional thermal polymerizations. The use of light provides spatial and temporal control of the reaction because it can be directed to a location of interest and stopped at a specified time. Several groups have described the preparation of monoliths for separations by UV photopolymerization [1, 2, 7, 8]. Free-radical polymerization is by far the most common approach toward the preparation of monoliths for separations [2, 9]. There are a variety of photoinitiators that produce free radicals upon absorption of UV light. In previous work [7], we have described the use of Irgacure 1800 (a mixture of a phosphineoxide derivative and an aryl ketone) as a UV photoinitiator in the preparation of organic–inorganic hybrid macroporous monoliths from methacrylate-functionalized alkoxysilanes. After hydrolysis and condensation (sol–gel chemistry) of the alkoxy groups in the silane monomer, a polymer was formed by UV-initiated free-radical polymerization of the methacrylate moiety. A disadvantage of this approach is the necessity to remove the polyimide coating surrounding the fused-silica capillary to create an irradiation window. Its removal renders the capillary fragile. Exploiting the spectral sensitivity of onium-salt photoinitiators in the visible region of the light spectrum, however, has allowed us to prepare macroporous hybrid monoliths using the same methacrylate-substituted alkoxysilane in a fused-silica capillary without removing its polyimide coating. This report describes the production of such sol–gel monoliths and how the properties of such monoliths vary with mobile phase composition, field strength, and column temperature.

The spectral response of onium-salt photoinitiators can be tuned from the short wavelength region of the UV spectrum to the visible region (from 330 to 650 nm) by using indirect activation, which involves electron transfer between an onium salt (On^+) and a photosensitizer (PS), as depicted in reaction 1 [10–16]. A titanocene PS, for example, can absorb visible light and then transfer its energy to the photoinitiator. Titanocene-based PS radical

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Abbreviations: APKs, alkyl phenyl ketones; **DPI,** diphenyliodonium chloride; **MPTMS,** methacryloxypropyltrimethoxysilane; **PS,** photosensitizer; **vis-PSG,** visible photopolymerized sol–gel

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cations have been shown to be useful free-radical promoters in photoinitiated cationic polymerizations [10–16].

$$PS^{*} + On^{+} \rightarrow PS^{+\bullet} + On^{\bullet} \quad (1)$$

We describe here the use of a titanocene/diarylonium salt photosystem for the preparation of a visible photopolymerized sol–gel (vis-PSG) using visible light. The photosensitization of diarylonium salts makes it possible to carry out *in situ* photoinitiated cationic polymerization of a methacrylate-substituted alkoxysilane in the visible region inside a polyimide-coated fused-silica capillary. To the best of our knowledge, the use of visible light to induce the polymerization of silane monomers has not been reported before. The vis-PSG has a porous structure and the ability to separate low-molecular weight neutral compounds in a liquid stream by application of an electric field.

2 Materials and methods

2.1 Chemicals and materials

Fused-silica capillaries (75 μm id × 365 μm od) were purchased from Polymicro Technologies (Phoenix, AZ). Methacryloxypropyltrimethoxysilane (MPTMS), diphenyliodonium chloride (DPI), HPLC-grade toluene, ACN, ethanol, and alkyl phenyl ketones (APKs) were purchased from Sigma–Aldrich (Milkwaukee, WI) and used without further purification. Irgacure 784 was received from Ciba (Tarrytown, NY).

2.2 Polymerization procedure

The sol–gel solution was prepared as follows. First, a mixture of 575 μL MPTMS and 100 μL 0.12 N HCl was stirred in the dark for 30 min at room temperature. A second solution (Solution 1) was prepared by mixing a specified volume of toluene with a specified volume of the MPTMS/HCl mixture, as indicated in Table 1. Solution 1 was added to a 1 mL glass vial containing preweighed Irgacure 784 and DPI. The contents of the vial were stirred in the dark for 5 min at room temperature. The resulting solution is monophasic with a dark orange color. Next, a specified volume of toluene was added to the vial according to Table 1; the solution was stirred in the dark for 5 min at room temperature. To the resulting single-phase solution a specified volume of the MPTMS/HCl solution was added according to Table 1. The final volume of the reaction solution is 560 μL containing 1.0 mmol Irgacure 784 and 1.5 mmol DPI. This final reaction solution was flowed through a 30-cm capillary using a 0.5 mL disposable tuberculin syringe and a hand-held vise. The capillary was then filled with this solution and its ends were sealed with parafilm plugs. A 10 cm section in the center of the capillary was exposed to 460 nm light from a homebuilt light box. The remaining sections of the capillary were masked with black tubing to prevent light from polymerizing the reaction solution in these areas. The irradiation times varied from 15 to 30 min.

Unreacted starting materials and alcohol byproducts were removed by rinsing the monolithic capillary with approximately 150 μL ethanol using a 0.5 mL disposable tuberculin syringe and a hand-held vise. Once unreacted materials were rinsed from the capillary, the monolith became opaque and could be viewed clearly through the polyimide coating of the capillary without the aid of a microscope. The uniformity of the resulting vis-PSG monolith was confirmed by examination at 100 × magnification.

The monoliths were not allowed to dry out to avoid shrinkage, cracking, and/or void formation within the monoliths. During use, monoliths were kept wet with the mobile phase. The monoliths were stored in either ethanol or ACN and the ends seals when the monoliths are not in use.

2.3 CEC

A detection window was prepared by removing a few millimeters of the polyimide coating with fuming H_2SO_4

Table 1. Reaction solution variations

Column	% Toluene v/v	Solution 1		Toluene[a] (μL)	MPTMS/HCl[b] (μL)
		Toluene (μL)	MPTMS/HCl (μL)		
A	60	260	140	80	80
B	66	292	108	80	80
C	68	300	100	80	80
D	71	320	80	80	80
E	75	360	40	80	80

a) Added to Solution 1 after mixing.
b) Added to the Solution 1–toluene mixture after mixing.

immediately after the monolith section. The monolithic capillary was installed into a Beckman P/ACE 5000 capillary cartridge. The monolithic capillary was conditioned by continuously flowing mobile phase through it for approximately 10 min using a syringe and a hand-held vise. The monolithic capillary was placed in a Beckman P/ACE 5000 instrument and was conditioned further by flowing the mobile phase at 20 psi, followed by electrokinetic conditioning at 5 kV for 30 min. Although the flow is low, we find it to be sufficient for this purpose.

The APK analytes were prepared in the mobile phase to prevent gradient effects during the CEC experiments. Mobile phases were made of various ratios (by vol.) of 10 mM ammonium acetate (pH 6.5), water, and ACN. A new sample solution was used for every injection to maintain the same concentration of ACN in the sample solution and mobile phase.

2.4 Instrumentation

A Beckman P/ACE 5000 CE instrument equipped with a UV-absorbance detector was used in all experiments. A homebuilt light box was equipped with four 15 W cool white fluorescent lamps. Blue-purple cellophane paper was placed over the fluorescent lamps as a bandpass filter to allow predominantly 460 nm light to fill the light box.

2.5 Morphology characterization

The morphology of a vis-PSG monolith was studied using SEM. Crosssectional segments of a monolithic capillary were imaged by SEM after sputtering with gold.

3 Results and discussion

3.1 Visible photopolymerization of a sol–gel solution

First MPTMS undergoes two steps [7], as shown in Eqs. (2–4). In the presence of an acidic catalyst, the alkoxy portions of the MPTMS monomer undergo hydrolysis and condensation reactions take place that are typical of sol–gel chemistry. During the hydrolysis and condensation reactions larger units (oligomers) of the MPTMS monomer are formed, but the reaction is not allowed to go to completion to form a glass-like sol–gel material.

Hydrolysis

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \quad (2)$$

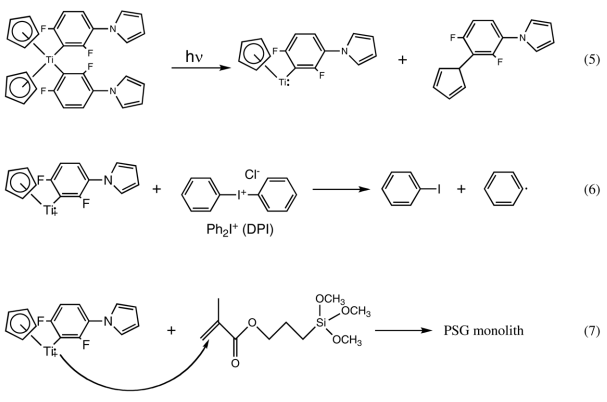
Condensation

$$2(RO)_3SiOH \rightarrow RO_3Si{-}O{-}Si(OR)_3 + H_2O \quad (3)$$

$$RO_4Si + (RO)_3SiOH \rightarrow (RO)_3Si{-}O{-}Si(OR)_3 + ROH \quad (4)$$

It might be wondered whether acid-catalyzed hydrolysis of methacrylate is important under our conditions. A search of the literature [17, 18] shows such effects, but they require a much longer time than our mixture is exposed to acid.

Next, the synthesis of the monolith involves photopolymerization of a mixture containing toluene (porogen) as well as the oligomers and the monomer. We have successfully prepared monoliths from the MPTMS monomer in capillaries using UV light, but a stripe of the polyimide coating on the capillary was removed to allow the light to enter the reaction solution through the glass [7]. When this stripe of polyimide is removed the mechanical strength of the capillary is reduced and the capillary is prone to breakage during its handling. Attempts to use commercially available UV-transparent coated capillaries were unsuccessful because the mechanical strength of these capillaries is poor. Furthermore, the coolant used in our CEC instruments is not compatible with the UV-transparent coating. Polyimide has a poor transmission of visible light (see http://www.luxel.com/std_fil_trans.htm for information on polymide transmission as a function of wavelength) but meets the mechanical strength requirements that make it so useful as a cladding material for capillaries. A photoinitiating system comprising Irgacure 784, a commericial titanocene-type PS that has a broad absorption between 400 and 500 nm, and DPI are used to allow visible light to initiate the photopolymerization of the monomer and oligomer units. It has been reported that titanocene/onium salt photosystems follow a free-radical promoted cationic polymerization mechanism [16, 19]. Irgacure 784 absorbs light at 460 nm where there is no spectral response from the oxidant, DPI. With the absorption of visible light by Irgacure 784, a titanium-centered diradical is produced according to Eq. (5). A transfer of an electron from the titanium-centered diradical to Ph_2I^+ (*i.e.*, DPI) yields a radical cation (Eq. 6.), which catalyzes the polymerization of the methacrylate groups (Eq. 7). Both components of the photosystem are necessary for the polymerization to occur. No polymer is formed in the absence of one of these compo-



nents under our reaction conditions, even after 180 min of irradiation.

Curable formulations of MPTMS were highly dependent on the solubility of the photosystem components in the reaction solution. Because Irgacure 784 is hydrophobic, it has limited solubility in the water-containing reaction mixture. On the other hand, DPI is soluble in water, but not in the organic portion of the reaction mixture. The composition of the reaction solution must be carefully varied to achieve a monophasic solution.

A variety of different organic additives were introduced to the reaction solution to aid in the solubility of the photosystem components. Although the addition of acetone, ACN, ethanol, dichloromethane, or DMSO improved the solubility of the components, a monophasic reaction solution was still not achieved. The addition of tetraethylammonium *p*-toluenesulfonate to a reaction solution that also contained one of the organic additives afforded a single-phase reaction solution, but no monolith is formed during irradiation of the solution in a capillary. In a different single-phase formulation, toluene and 4-(methylsulfonyl)benzene were used as coporogens, but no monolith is formed during irradiation of the resulting monophasic reaction solution.

Finally, a mixing procedure was developed to ensure that the appropriate concentrations of Irgacure 784 and DPI are soluble in the original reaction mixture. First, a specified volume of toluene is added to a mixture of MPTMS/HCl after stirring to afford a single-phase dark orange solution. Second, more toluene is added to this solution. Finally, more of the MPMTS/HCl solution is added to the reaction solution. By slowly adding the organic and aqueous portions of the reaction mixture in parts, the final reaction solution is maintained as monophasic. Table 1 summarizes the different formulations that were studied.

A single-phase reaction solution is expected to result in a more uniform and reproducible vis-PSG monolith for the separation of our test mixture. Peak fronting was observed from a monolith prepared with a cloudy reaction solution containing five times the amount of Irgacure 784 and DPI and either 60 or 68% toluene (data not shown). The peak fronting is likely caused by a nonuniform monolith. It can be postulated that there may be a problem with the physical structure of the monolith, such as a void at the head of the monolith, channeling within the monolith, or a less dense bed structure along the capillary walls as compared to the middle portion of the monolith. As a portion of the analyte molecules travels through the less dense part of the monolith, for example, the analytes will travel more quickly, distorting the peak. If the bulk of the peak is retained normally, fronting of the peak will occur. Because the test analytes do not contain any basic groups, fronting of the peaks is not likely to be explained by interaction of the analytes with the acidic silanol groups on the monolith.

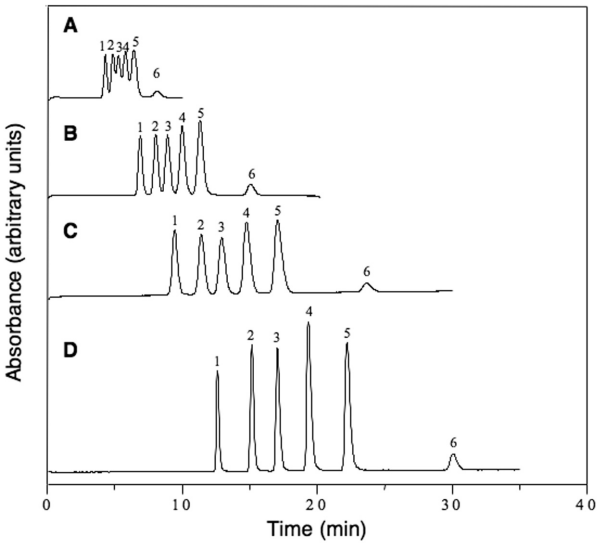


Figure 1. Electrochromatograms of the separation of six APKs on monoliths made with (A) 75% (column B), (B) 71% (column C), (C) 68% (column D), and (D) 66% (column E) v/v toluene and 15 min of irradiation with visible light. The elution order of the ketones is propiophenone (1), valerophenone (2), hexanophenone (3), heptanophenone (4), octanophenone (5), and decanophenone (6). Sample solution and mobile phase, 10 mM ammonium acetate (pH 6.5)/water/ACN (1:4:5); 0.5 psi pressure injection, 3 s; applied voltage, 20 kV; temperature, 20°C; detection, 254 nm.

Thermally activated polymerization of MPTMS is not observed in the masked areas of the capillary. Thermally initiated polymerization in the presence of Iragacure 784 occurs above 140°C [20].

Figure 1 presents the separation abilities for a sample of six APKs in four columns containing different vis-PSG monoliths. In all four columns, the elution order of each monolith follows an RP mechanism with the smallest molecular weight or the least hydrophobic (propiophenone) eluting first and the largest molecular weight or most hydrophobic (decanophenone) eluting last. Baseline separation of the APKs is achieved when the column is made with 71% (Fig. 1B, column D), 68% (Fig. 1C, column C), and 66% (Fig. 1D, column B) v/v toluene. With a decrease in the porogen concentration, the permeability of the column decreases, and there is a concomitant increase in the volume of the monomer in the reaction solution so more of the photopolymer is formed with which the analytes can interact [7]. The highest retention of analytes on the vis-PSG surface and, therefore, the best separation is shown for column E (Fig. 1D) where all six analytes are eluted within 31 min. Less photopolymer is formed in column B because of a lower concentration of the monomer in the reaction solution. As a result there is

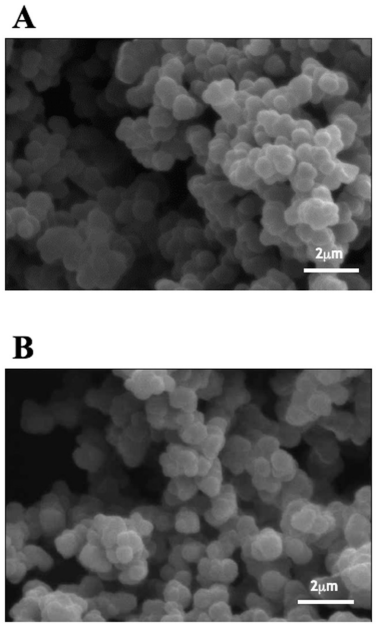


Figure 2. Scanning electron micrographs of (A) the crosssection of a vis-PSG photopolymer formed with 68% v/v toluene (column C) in a 75 μm-id capillary column and (B) the crosssection of a vis-PSG photopolymer formed with 71% v/v toluene (column C) in a 75 μm-id capillary column.

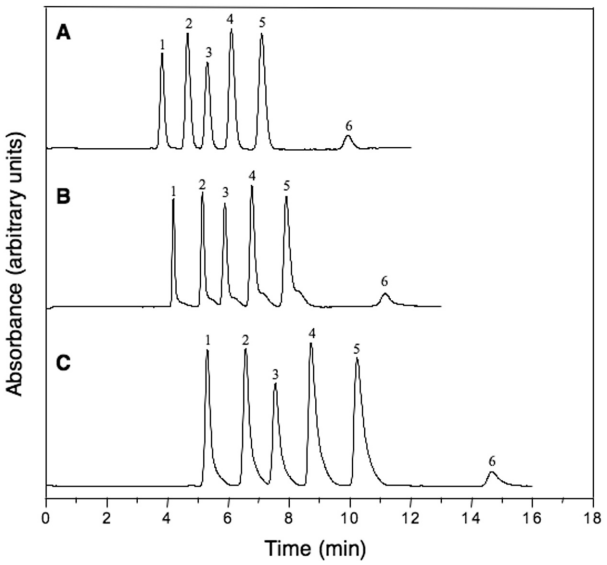


Figure 3. Electrochromatograms of the separation of six APKs on vis-PSG photopolymers (68% v/v toluene) made at a polymerization time of (A) 15, (B) 20, and (C) 25 min. The elution order of the ketones is propiophenone (1), valerophenone (2), hexanophenone (3), heptanophenone (4), octanophenone (5), and decanophenone (6). The applied voltage was 30 kV. All other conditions are the same as in Fig. 1.

lower retention of the analytes on the vis-PSG surface, and separation of the analytes is poor, as shown in Fig. 1A.

We have made a comparison of the performance of the vis-PSG monolith with that of the UV-PSG, and we find them to be comparable. We do note that the vis-PSG monolith takes longer (15 min compared to 5 min) to prepare than the UV-PSG monolith but the former might be sped up by using a higher light intensity.

The separation performance of the vis-PSG monolith seems to depend sensitively on the porogen concentration used in making it. Characterization of vis-PSG formed with 68% (column C) and 66% (column D) v/v toluene by SEM reveals an interconnecting network of clusters of nearly spherical structures that are 2 μm in diameter or less through which micron-sized macropores are interspersed (see Fig. 2). Although these images are nearly identical in morphology, their separation abilities are quite different (as shown in Figs. 1C and D). SEM analyses (not shown) also reveal that both monoliths are bonded to the capillary walls.

Photopolymerization of the reaction solution at different irradiation times has an effect on the separation performance of the resulting vis-PSG monolith. With the porogen volume kept constant at 66% v/v, three different monoliths were prepared at 15-, 20-, and 25 min irradiation times. Figure 3 compares the RP separation of a mixture of six analytes on each of these three monoliths. The baseline separation of the APKs is best for the monolith prepared at 15 min irradiation time as illustrated in Fig. 3A. Furthermore, the peak shapes are symmetrical. Figs. 3B and C show peak tailing for all the analyte peaks eluted from a monolith prepared at 20 and 25 min irradiation times, respectively. The asymmetry of the peaks for the latter two monoliths may arise from structural changes within the monolith during the longer irradiation time that leads to nonuniformity. Furthermore, the retention times of the analytes in Fig. 3C are longer than for the analytes shown in Fig. 3B, suggesting that more photopolymer was formed during the longer irradiation time with which the analytes can interact. The symmetrically shaped peaks appearing in Fig. 3A suggests that this monolith is uniform in structure.

The separation performances of the vis-PSG monoliths were evaluated at higher field strengths of 778, 973, and 1167 V/cm than are typically used in CEC. At such high field strengths, it is expected that peak broadening will occur as a result of Joule heating. It appears that the Joule heat generated at these high field strengths is dissipated efficiently such that peak broadening is not observed. The linearity (R = 0.99994) of the current with applied voltage in the range of 10–30 kV suggests that there is little heating effect in the vis-PSG capillary column.

Reproducibility from run-to-run and column-to-column on a vis-PSG monolith (column C) was determined under identical run conditions. The RSD values (n = 5) from run-to-run on a single column for the migration

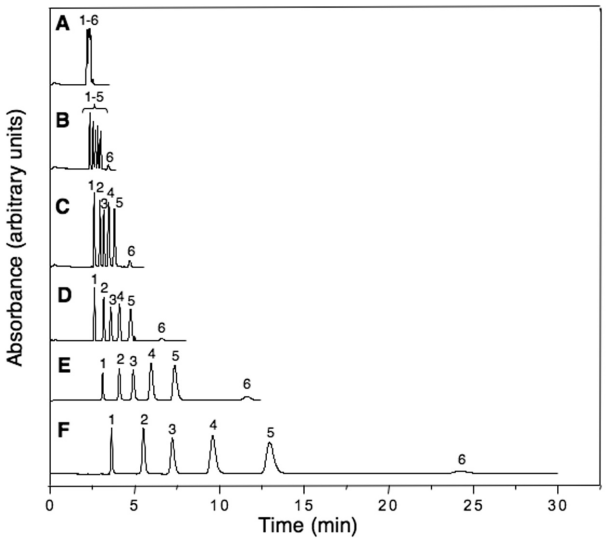


Figure 4. Electrochromatograms of the separation of APKs on vis-PSG column C with ACN concentrations of (A) 70, (B) 60, (C) 55, (D) 50, (E) 45, and (F) 40% in the mobile phase. The elution order of the analytes is propiophenone (1), valerophenone (2), hexanophenone (3), heptanophenone (4), octanophenone (5), and decanophenone (6). The applied voltage is 30 kV. All other conditions are similar to those in Fig. 1.

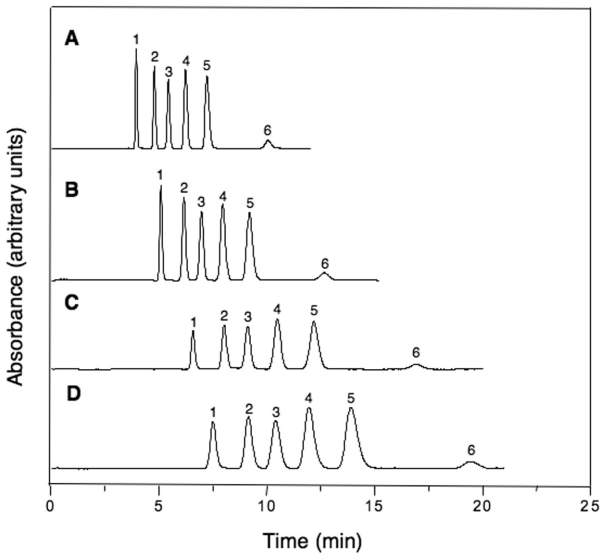


Figure 5. Electrochromatograms of the separation of APKs on vis-PSG column D with buffer concentrations of (A) 1.0, (B) 2.0, (C) 2.5, and (D) 3.0 mM in the mobile phase. Conditions are the same as in Fig. 1.

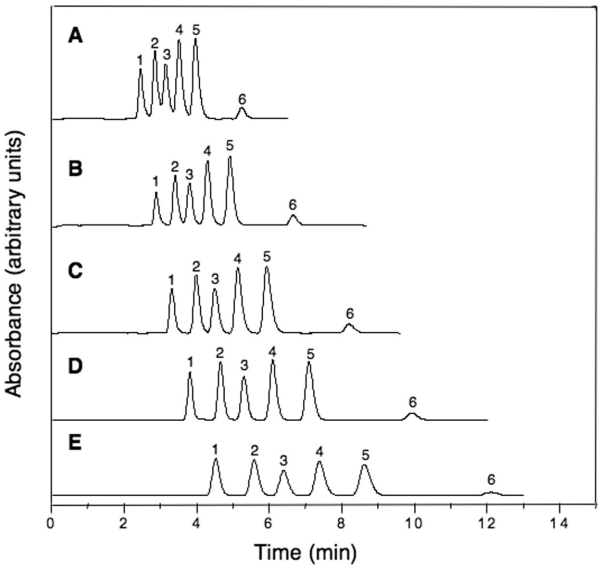


Figure 6. Electrochromatograms of the separation of APKs on vis-PSG column D at run temperatures of (A) 50, (B) 40, (C) 30, (D) 20, and (E) 12°C. Conditions are the same as in Fig. 1.

times of propiophenone, valerophenone, hexanophenone, heptanophenone, octanophenone, and decanophenone are 0.75, 0.83, 0.90, 0.99, 1.07, and 1.20%, respectively. The RSD values ($n = 4$) from column-to-column for the migration times of propiophenone, valerophenone, hexanophenone, heptanophenone, octanophenone, and decanophenone are 1.27, 1.51, 1.80, 2.29, 2.67, 3.68%, respectively.

3.2 Effects of operational parameters on separation

Figure 4 illustrates the dependence of the selectivity of the monolith (column C) for a series of six APKs on the ACN concentration in the mobile phase, which is expected for an RP mechanism where the elution times decrease with an increase in organic solvent concentration in the mobile phase. The ACN composition of the mobile phase is in the range of 40–70% v/v. At 70% v/v ACN, Fig. 4A shows that the analytes are coeluted. Some separation of the analyte peaks is observed for ACN concentration of 60% v/v (Fig. 4B) and 55% (Fig. 4C). At 40–55% v/v ACN, baseline separations of all six APKs are achieved, with the peak shapes being symmetrical (Figs. 4D–F).

We studied the effect of ionic strength for ammonium acetate (pH 6.5) buffer concentrations between 1 and 3 mM containing 50% ACN. As the ionic strength of the buffer in the mobile phase is increased, the elution times are increased as illustrated in Fig. 5. A linear relationship is established between the ionic strength and the elution times at the buffer concentration range studied as is expected for CEC separations [21]. The longest separation time is illustrated in Fig. 5D for a buffer concentration of 3.0 mM where the APKs are eluted just under 20 min. The peak widths of the analytes, however, increased as the buffer concentration in the mobile phase increased suggesting that high electrolyte concentration can give

rise to Joule heating, which can lead to band broadening of the analyte peaks [22].

Figure 6 illustrates that as the column temperature is increased to 50°C, the elution times of the analytes decreased as the EOF velocity increased. The analyte peaks are eluted within 6 min at 50°C (Fig. 6A) while at 12°C (Fig. 6E) the analytes are eluted within 12 min. Increasing the column temperature in CEC increases the EOF velocity for a given voltage and decreases the retention times because the mobile-phase viscosity falls. Peak widths are similar in the 20–50°C temperature range while the peak widths become broader at a run temperature of 12°C. At low temperature, the EOF velocity is lower such that the solute bands remain in the column longer. As a result, longitudinal diffusion is likely to be greater at 12°C *versus* temperatures between 20 and 50°C, and this could lead to increased band broadening of the solute peaks [23], although the effects of temperature on mass transport cannot be excluded. RSD values for the retention times of the analytes at the different run temperatures vary from 0.3 to 1.1%.

4 Concluding remarks

The titanocene Irgacure 784 and DPI are effective photosensitizer and photoinitiator, respectively, for the visible light-initiated photopolymerization of a mixture of methacrylate-substituted alkoxysilane, acid catalyst, and porogen in a polyimide-coated fused-silica capillary. The resulting photopolymer behaves as an RP chromatographic material and is able to efficiently and reproducibly separate a mixture of small, neutral organic compounds. We conclude that visible light may be successfully used to initiate photopolymerization of sol–gel solutions for the purpose of constructing *in situ* macroporous monoliths in polyimide-coated capillaries.

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