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Effect of precursor macromonomer molecular weight on poly(dimethylsiloxane) film morphology and nitroaromatic vapor sorption

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ABSTRACT

The capability to detect nitro-based explosives from their vapor is often limited by their low vapor pressure. One approach for overcoming this limitation is to use a solid-state pre-concentrator. The sorption and desorption of nitroaromatic vapors by poly(dimethylsiloxane)-based (PDMS) films fabricated from three different molecular weights of hydroxy-terminated poly(dimethylsiloxane) (HO-PDMS) macromonomers has been investigated. It was found that independent of macromonomer molecular weight, all the PDMS films were able to sorb nitro-based explosive analyte. However, for PDMS films of similar thickness, those formed from the lowest molecular weight macromonomer sorbed the least analyte and had the poorest retention capability. Atomic Force Microscopy (AFM) suggested that at least a proportion of the analyte was adsorbed onto the surface of the PDMS film formed from the low molecular weight macromonomer. PDMS films from the higher molecular weight macromonomers sorb more analyte with the vapor diffusing into the bulk of the film. PDMS films formed from the 750 cSt macromonomer were found to have the best analyte sorption and retention properties. The best pre-concentrator film was determined to increase the available analyte for vapor detection by up to 2 orders of magnitude.

1. Introduction

Explosive devices continue to cause devastation, with loss of life and injury, and damage to property through terrorist acts and unexploded ordinance such as landmines [1,2]. Furthermore, the toxicity of many explosives can also lead to long-term health issues for humans and contamination of the environment [3,4]. To counter the threat posed by explosive devices, reliable detection is of upmost importance. Among the methods of explosive detection, vapor sensing remains one of the most attractive options because it enables non-invasive searching and stand-off sensing [5]. Unfortunately many high explosives, including nitroaromatics, nitramines, and nitrate esters are difficult to detect because they have low volatilities with vapor pressures ranging from parts per billion (ppb) to parts per trillion (ppt) [6]. The low volatility of the analytes is a key factor that currently constrains the performance of vapor-based detectors for stand-off detection. One solution to the low volatility problem is to use a pre-concentrator to effectively increase the amount of the vapor delivered to the sensing element. Solid-phase microextractors (SPMEs) have been developed to pre-concentrate samples and are often used to collect samples for Gas Chromatography, with the latter providing the selectivity for identification of the analyte. SPMEs sorb the sample over a period of time with the concentrated sample released by heating, which provides a pulse or packet of the analyte to the sensing device. Polydimethylsiloxane (PDMS) and PDMS:1,4-divinylbenzene (DVB) have been used as the active sorber of SPMEs for pre-concentration of analytes in the molecular weight range of ≈50–300 amu [7]. In particular, SPMEs comprised of either PDMS or PDMS:DVB have been investigated for the pre-concentration of nitro-based explosive compounds, with the latter material showing the greatest pre-concentration capability based on released material [8].

Designing the sorbing material for analyte extraction is important for the development of pre-concentrators. The sorbing materials are required to have: good analyte affinity, high absorption capacity, fast sorption-desorption capability under specific conditions (the sorbed material must remain in the pre-concentrator material until the releasing conditions are applied), and good thermal stability [9]. PDMS was one of the earliest sorbing materials used, both in terms of research and in commercial pre-

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concentrator devices [7]. PDMS can sorb a wide range of analytes, which is attributed to its porous structure, polyvalent trapping properties, and thermal stability that allows field sampling [10]. PDMS is often produced via a sol-gel process from macromonomers of differing molecular weights. It might be thought that the macromonomer molecular weight would only have a minor effect on the properties of the as-formed PDMS. However, studies have shown that the molecular weight of the macromonomer can affect the Young's modulus [11], wettability/surface energy [11,12], and adhesion and friction [13] of the PDMS.

In this work, we study the effect of the macromonomer molecular weight on the uptake and subsequent release of nitroaromatic vapor from PDMS films fabricated using a sol-gel method. The sol-gel method was chosen because it is known to improve the bonding of the film to the substrate compared to the commercially fabricated PDMS microextractors, which results in better thermal and chemical stability [14,15]. In particular, we show that good quality transparent PDMS films can be produced by the sol-gel method, which enables absorption spectroscopy to be used to quantify the uptake and retention of the analyte.

2. Experiment

2.1. Reagents

All chemicals were acquired from commercial suppliers and were used as received, unless otherwise stated. Hydrogen peroxide (30% H_2O_2) and sodium hydroxide (NaOH) were purchased from Chem-Supply Pty Ltd while sulfuric acid (98% H_2SO_4), hydrochloric acid (97% HCl) and methyltriethoxysilane (MTEOS) were purchased from VWR International S.A.S., Ajax Finechem Pty Ltd, and Alfa Aesar Inc., respectively. Three hydroxy-terminated poly(dimethylsiloxane) (HO-PDMS) macromonomers with different viscosities and molecular weights (*Mw*) of 25 cSt (400–700 g/mol), 750 cSt (18,000 g/mol) and 18,000–22,000 cSt (75,000 g/mol) were purchased from Sigma-Aldrich, Co. The molecular weights were obtained from the manufacturer. Poly(methylhydrosiloxane) (PMHS) (*Mn*: 1700–3200 g/mol), trifluoroacetic acid (99% TFA), dichloromethane (DCM) and 3 Å molecular sieves were also obtained from Sigma-Aldrich, Co. The DCM was distilled and stored over activated 3 Å molecular sieves before use. 4-Nitrotoluene (pNT), 2,4-dinitrotoluene (DNT), and 1,4-dinitrobenzene (DNB) were purchased from Sigma-Aldrich Co., while 2,4,6-trinitrotoluene (TNT) was provided by Defence Science and Technology Group (Edinburgh, Australia).

2.2. Preparation of substrates

Prior to PDMS film fabrication the fused silica substrates (12 mm diameter) were chemically treated to achieve the maximum possible number of surface silanol groups for polymer-substrate bonding. The substrates were sonicated in acetone for 10 min, rinsed with distilled water (5 × 20 mL) and dried in an oven at 120 °C. The pre-cleaned substrates were soaked in Piranha solution [hydrogen peroxide (30%, 3 mL) and sulfuric acid (18 M, 9 mL)] for about 1 h while heated at 90 °C, to remove any organic residue. The substrates were then washed with distilled water (5 × 20 mL) before being soaked in aqueous sodium hydroxide (1 M) for 1 h. The treated substrates were rinsed with distilled water (5 × 20 mL) and soaked in hydrochloric acid (0.1 M) for 30 min. Finally, the substrates were washed with distilled water (5 × 20 mL) and dried in an oven at 120 °C.

2.3. Film fabrication

The sol-gel precursor solution was composed of the macromonomer (HO-PDMS), cross-linker (MTEOS), polymerization-terminating polymer (PMHS), solvent (DCM), and an acid catalyst (95% TFA). The solution was prepared following the method described in Ref. [16] with a slight modification in the mixing process. MTEOS was used instead of tetraethoxysilane (TEOS) as it has been shown to suppress film cracking and proceeded with a faster reaction rate [17]. Taking the optimized ratio from the literature; HO-PDMS (1.5 mL of different viscosities), MTEOS (1 mL, 5 mmol) and PMHS (0.1 mL, average of 0.045 mmol) were dissolved with DCM (1.5 mL). The solution was sonicated for 5 min to facilitate mixing of the components. TFA (95%, 0.4 mL) was then added followed by sonication for another 5 min. The clear solution was then used immediately for dip-coating. The precursor solution was coated onto both sides of the fused silica substrates using a Xdip-SV1 dip-coater. The sol-gel precursor solution was poured into a metal container (20 mm deep), which was capable of holding around ≈2 mL solution. The cleaned fused silica substrates were held by the edge and the holder also had a cover such that when the substrate was immersed in the solution the container was covered, thus minimizing the loss of volatile components. The substrate was lowered into the sol solution at a constant rate of 50 mm/min and held for 5 min. After soaking, the substrate was withdrawn at a constant speed of 50 mm/min and left to dry in air for 12 s. To increase the thickness of the film, the number of dip-coating cycles was varied between 1, 3, 5 and 7 before the final drying of the films. The finished coated substrates were dried in an oven for 24 h at 60 °C. Finally, the dried films were annealed at 250 °C under high vacuum for 3 h to remove remaining volatiles and pre-condition the films so no subsequent morphological changes due to temperature occurred during the measurements.

2.4. Film characterization

Infrared spectra were collected using a PerkinElmer Spectrum 1000 Fourier Transform Infrared (FTIR) spectrometer. The thermal stability of the films was determined using a PerkinElmer Simultaneous Thermal Analyzer (STA) 6000. The thickness of the films was determined using a Veeco Dektak 150 surface profiler. The surface topology of the as-cast films, and their evolution upon analyte uptake and release were measured using a Cypher Atomic Force Microscope (AFM). The AFM measurements were performed twice at two points per sample in air in tapping mode utilizing an Etalon cantilever of 10 nm diameter.

2.5. Analyte vapor sorption/retention

The analyte sorption capability of films of different thickness in the absence and presence of the analyte was investigated using a Cary 5000 UV–vis-NIR spectrophotometer. To measure the quantity of analyte sorbed by the films, analyte (pNT, DNT, DNB, or TNT) vapor chambers were prepared using 15 mL capped glass vials. Each of the vials were filled with 5 mg of the desired analyte, with solids of pNT, DNT and DNB weighed out, and in the case of TNT, 0.7 mL of TNT in acetonitrile solution (7.5 mg/mL) was measured and left to dry. The analyte was covered with cotton wool to prevent direct contact between the analyte and the sample. The vials were left to equilibrate at room temperature for at least 2 h before the samples were introduced. The PDMS films were placed in saturated vapor for 1, 5, 15, 25, 60, 90, or 120 min or overnight. The amount of analyte sorbed by the film was determined from the change in optical density relative to the as-cast film. The change in the optical density was converted to moles using the Beer-Lambert Law. Details of the calculation are provided in the Supplementary Information.