

Properties of PDMS-Divinylbenzene Based Pre-concentrators for Nitroaromatic Vapors

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Supporting Information

1. Characterization of the films

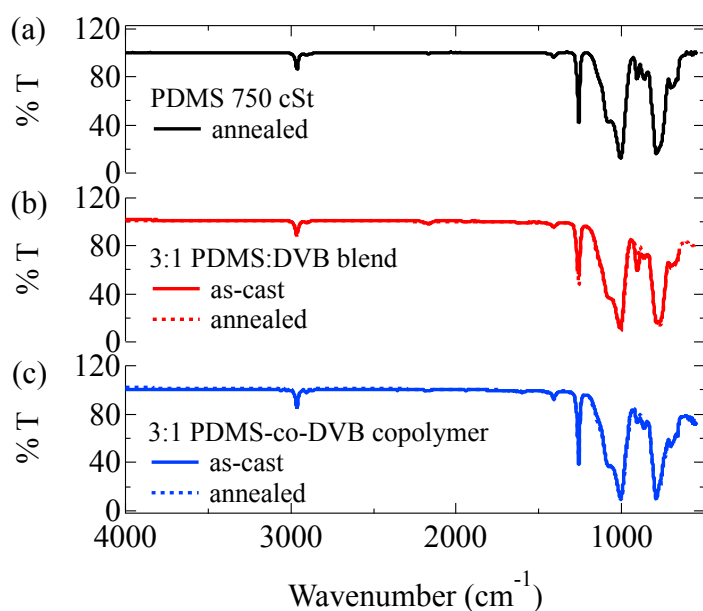


Figure S1. Infrared spectra of (a) pristine PDMS, (b) 3:1 PDMS:DVB and (c) 3:1 PDMS-co-DVB as-cast and annealed films.

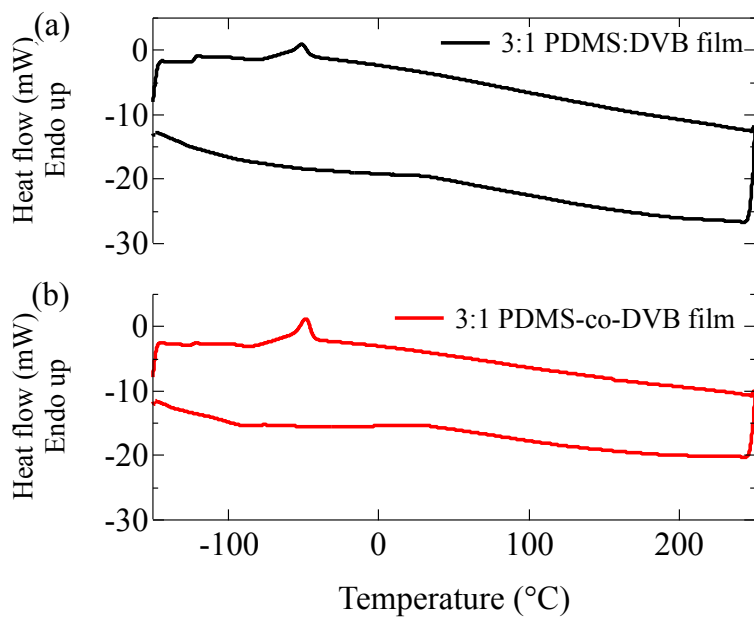


Figure S2. Heat flow (Endo up) plot of (a) 3:1 PDMS:DVB and (b) 3:1 PDMS-co-DVB copolymer films. Three scans were carried out with only the 3rd scan shown in the figure as the same features appeared in all three scans.

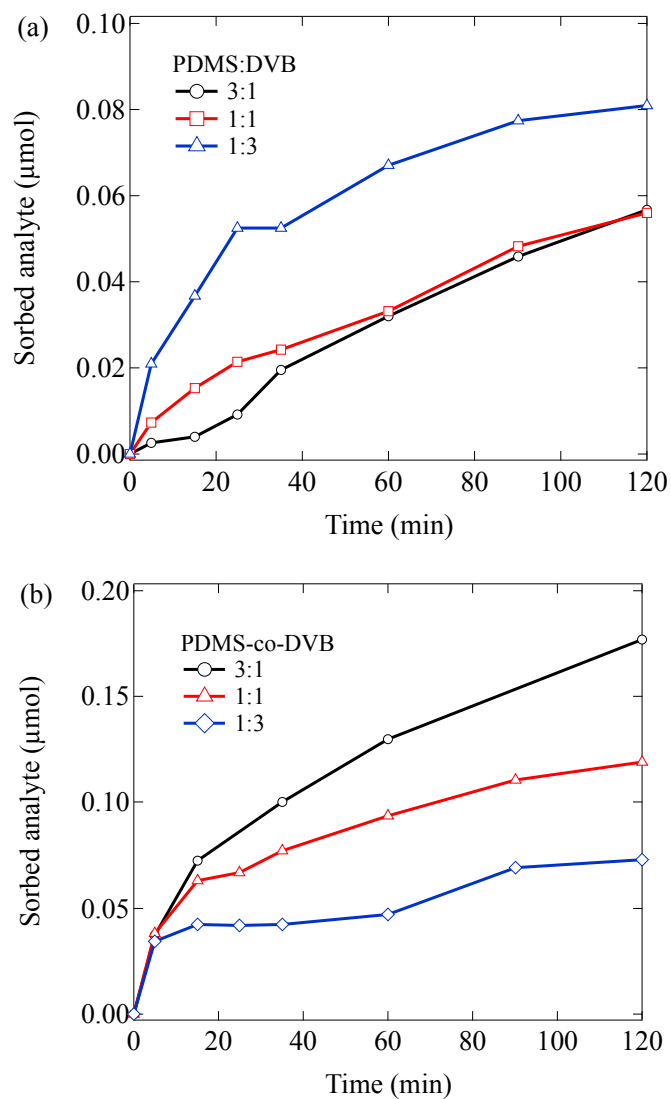


Figure S3. Change in the amount of *p*NT sorbed over time by (a) PDMS:DVB films (~13 μm) and (b) PDMS-co-DVB films (~13 μm) fabricated from different ratios of HO-PDMS and DVB.

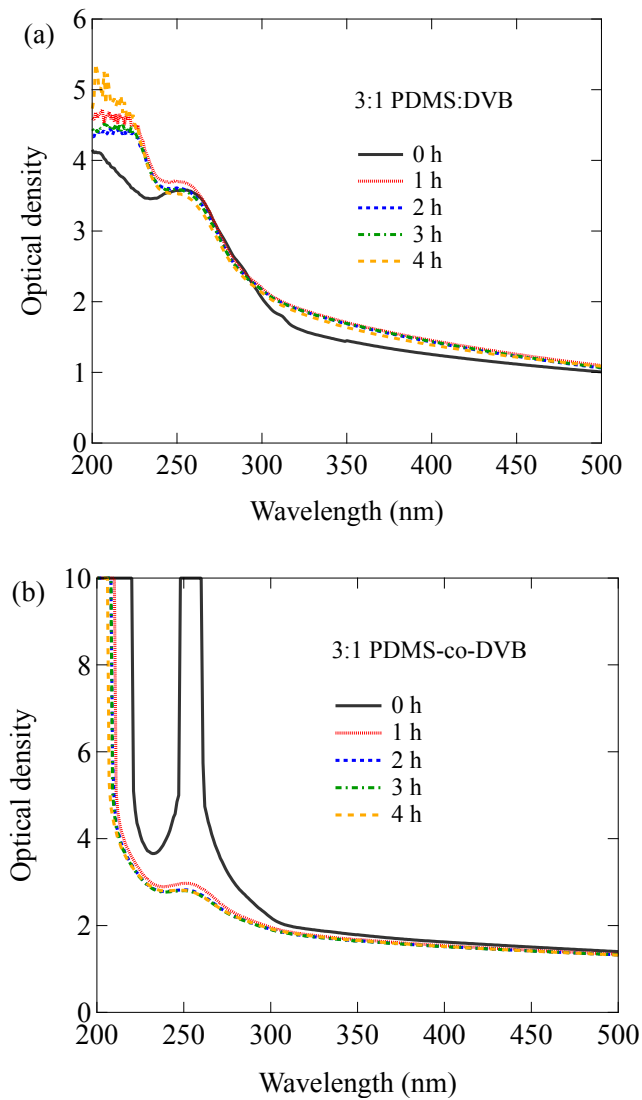


Figure S4. Absorption spectra versus time of $\sim 13 \mu\text{m}$ thick (a) 3:1 PDMS:DVB and (b) 3:1 PDMS-co-DVB films annealed at 250°C under vacuum over 4 h.

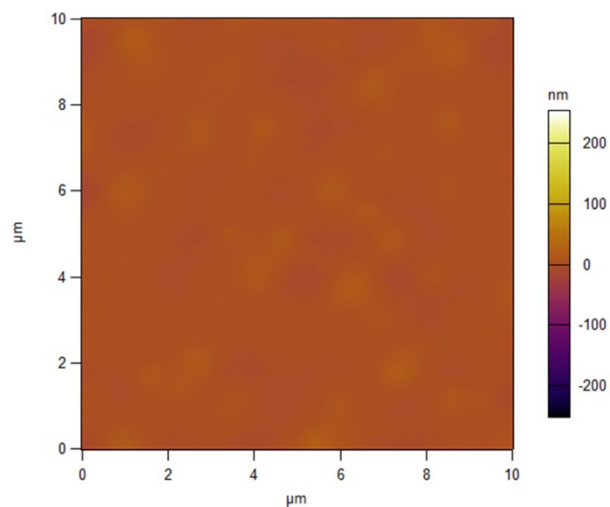


Figure S5. Surface morphology of the post-annealed PDMS film showing no pores.

2. Analyte vapor sorption

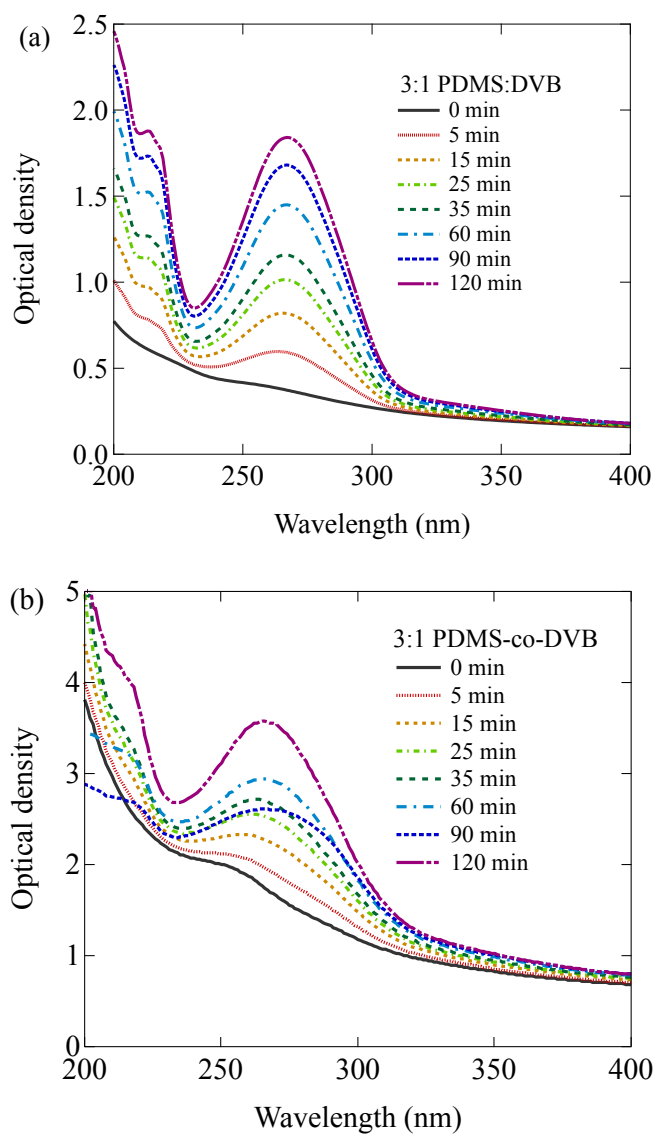


Figure S6. UV-Vis spectra of (a) $12.4 \pm 0.2 \mu\text{m}$ 3:1 PDMS:DVB blend and (b) $13.1 \pm 0.8 \mu\text{m}$ 3:1 PDMS-co-DVB films coated on one side of the fused silica substrate showing the increase in the optical density upon exposure of the films to *p*NT vapor.

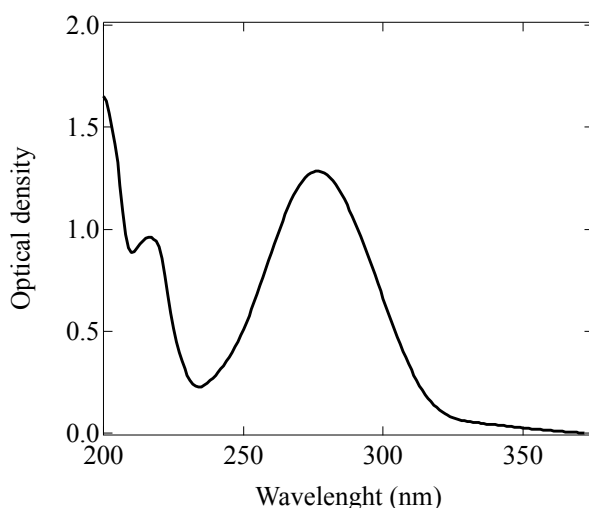


Figure S7. Absorption spectrum of 143 μM *p*NT in acetonitrile.

3. Calculation of the amount of analyte sorbed by the PDMS film expressed in moles

The amount of *p*NT, DNT and TNT sorbed by the PDMS films in moles was calculated from the optical density changes between the pristine and analyte-exposed films, with the latter considered as solid solutions of the analyte in the films. Firstly, the molar extinction coefficients of *p*NT, DNT, DNB and TNT were determined using a minimum of 5 known concentrations of each analyte in acetonitrile. The optical densities measured from the analyte solutions were plotted against their corresponding concentrations to check the linearity of the measurement. Standard deviation within the linear fit was carried over as the error in analyte sorption tests. For *p*NT, optical densities of 8 concentrations ranged from 1 to 3 with a linear regression = 0.99 and standard deviation of 3%. The molar extinction coefficients of the analytes were calculated using the Beer-Lambert Law

$$A(\lambda) = \varepsilon(\lambda)lc$$

where A is the absorbance, ε is the molar extinction coefficient, l is the optical path length (1 cm) and c is the concentration of the solution. The measured peak absorption molar extinction coefficients were; *p*NT ($\lambda_{\text{max}} = 269$ nm): $10,893 \pm 76$ L/mol-cm; 2,4-DNT ($\lambda_{\text{max}} = 240$ nm): $14,810 \pm 31$ L/mol-cm; TNT ($\lambda_{\text{max}} = 228$ nm): $29,782 \pm 99$ L/mol-cm.

The Beer-Lambert Law was used to determine the number of moles of analyte in the film, with A being the optical density change between the unexposed and analyte-exposed films, ε the molar extinction coefficient of the analyte from solution and l is the film thickness. Note that some films were coated on two sides of the substrates, in this case the measured A was halved so that the equivalent concentration of analyte in single coating could be calculated. The amount of analyte within the beam area was first determined and then scaled to the total volume of the film coated only

on one side of the substrate. The beam area (12.5 mm^2) was determined by measuring the width (2.5 mm) of the beam and multiplying it by the aperture diameter (5 mm) of the sample holder. The volume of the film was calculated using the area of the substrate (radius: 6.0 mm) multiplied to the thickness of the film. For thick films where the optical density was >3 at the analyte absorbance peak, the absorbance change between unexposed and analyte-exposed film was taken at 310 nm, with the corresponding molar extinction coefficient of the analyte determined for that wavelength.

4. Calculation of the effective concentration of pre-concentrated analyte

The effective concentration of pre-concentrated *p*NT, DNT and TNT was calculated from the amount of analyte sorbed by films of comparable thickness (e.g. 13 μm) exposed to an analyte for 2 h. Assuming complete release of the analyte from the film within 10 sec [as in gas chromatography (GC) or high-performance liquid chromatography (HPLC) at 250 °C] and a sampling flow rate of 30 mL/min, the amount of analyte released by the film will be diluted in a 5 mL of gas. For example, 0.6 μmol *p*NT sorbed in the film will have an effective concentration of 0.12 $\mu\text{mol/mL}$ within 10 sec desorption. To convert the unit of the effective concentration from $\mu\text{mol/mL}$ to ppm, the mole ratio of the analyte to the gas volume was first calculated. The mole ratio of the analyte relative to the atmosphere was calculated by multiplying the concentration in $\mu\text{mol/mL}$ with a (22400 mL)/mol conversion factor, assuming an ideal gas system. The concentration in mole ratio was then converted to ppm by multiplying the mole ratio by 1,000,000.