Journal of Applied Polymer Science

Development of Thin Layer Polymers to Concentrate and Detect Aquatic Contaminants

Rebecca A. Lyons,[1] John P. Hassett,[2] Anna M. Flach,[2] Israel Cabasso[3]

[1]University of Chemistry Department, Redlands, California 92373

[2]College of Environmental Science and Chemistry Department, State University of New York, Syracuse, New York 13210

[3]Polymer Research Institute, State University of New York, Syracuse, New York 13210

Correspondence to: R. A. Lyons (E-mail: Rebecca_lyons@redlands.edu)

ABSTRACT: Poly(dimethylsiloxane) (PDMS) and a poly(DMS-styrene) block copolymer were compared as extraction and optical detection media for hydrophobic compounds in water and water/ethanol solutions. Partitioning to both polymers increased exponentially with increased percent water in ethanol. Partition coefficients to the copolymer were 10–30-fold higher than to PDMS. Ultraviolet absorbance spectra of pyrene showed a 4-nm red-shift in copolymer versus PDMS, providing evidence of π–π interactions, accounting for greater partitioning. The extinction coefficient coefficient of pyrene at 334 nm was twice as high in the copolymer as in PDMS. The combination of higher affinity for polycyclic aromatic hydrocarbons with higher absorbance make poly(DMS-styrene) copolymers promising material for extraction and *in situ* detection of hydrophobic aromatic compounds in water. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: block copolymer; polystyrene; poly(dimethylsiloxane); partitioning

Received 24 March 2011; accepted 6 April 2012; published online
DOI: 10.1002/app.37857

INTRODUCTION

Trace hydrophobic organic compounds are not easily detected in aqueous systems. Many contaminants, such as polycyclic aromatic hydrocarbons (PAHs), occur in concentrations on the order of nanograms to picograms per liter. Contamination events in aquatic systems may occur on the scale of weeks, in the case of snow melt, to hours in the case of an oil spill, or other catastrophic event. Analytical methods that can be performed rapidly while delivering low detection limits are necessary for assessing and understanding the impact of these events. Solid-phase microextraction (SPME) methods offer such advantages.[1] SPME samplers take up organic compounds from a water sample into a polymer phase. The polymer is typically a thin film coated onto a fiber that can be inserted directly into conventional chromatographic injectors. Such syringe-like devices are commercially available and widely used. Methods that use polymer sheets with large areas and volumes to collect larger amounts of analytes have also been described.[2,3] In all SPME methods, the polymer film concentrates analytes from the sample, and analytes are later desorbed from the film for analysis. The ability to desorb the entire extract from the film into a chromatographic system gives SPME methods their low detection limits.

A variety of polymers have been explored as collecting phases for SPME applications,[1] but the most widely used for collection of hydrophobic compounds is poly(dimethylsiloxane) (PDMS). In this study, we successfully compare poly(DMS-styrene) block copolymer (Figure 1) with PDMS, as thin-film traps for PAHs in water solutions. PAHs were selected as analytes representative of a broader spectrum of hydrophobic compounds with aromatic moieties. PAHs are ubiquitous, toxic, and typify the behavior of aqueous, hydrophobic compounds.

Block copolymers in particular are interesting as they possess unique microstructure and have the potential to be tailored according to the properties of the individual components. To be successfully applied to SPME, the polymer should facilitate the partitioning of analyte from the bulk aqueous phase. It should also permit diffusion and permeability of analyte into the retention media. Both polystyrene and PDMS are considered hydrophobic and have been shown to adsorb polycyclic aromatic compounds.[4] PDMS, polystyrene, and their copolymers have

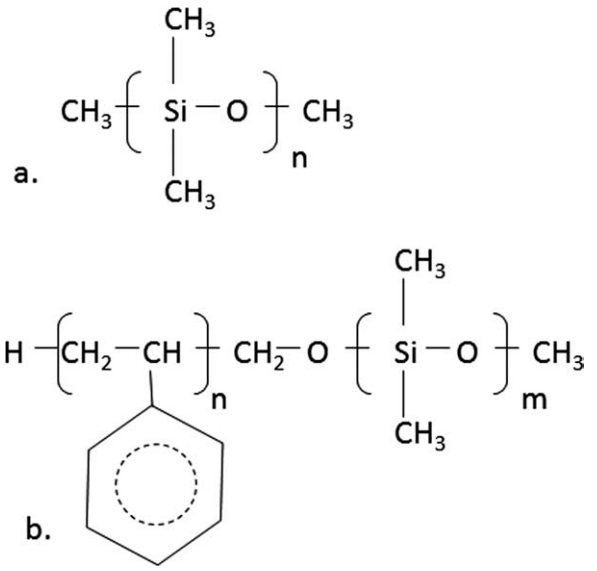

Figure 1. The repeating unit for (a) PDMS and (b) the poly(DMS-styrene) copolymer.

other desirable physical properties such as being chemically inert, easily manipulated into thin films, and relatively inexpensive.

In addition to acting as extraction media for hydrophobic compounds, PDMS and poly(DMS-styrene) films are optically transparent, making them potential media for direct spectroscopic detection of captured compounds.[5] Although this would be less specific than chromatographic analysis, it would allow rapid screening of samples by absorbance or fluorescence. In addition, we have recently shown that hydrophobic compounds can be extracted from water in an online system using ethanol and other water-miscible alcohols as solvents.[6] In this study, we examine the potential of PDMS and poly(DMS-styrene) to trap hydrophobic compounds from ethanol solutions after addition of various amounts of water. These films fulfill a parallel role as matrices for optical detection and quantification of hydrophobic compounds. Their capacities in this respect are assessed by measuring molar absorbance of compounds in the polymer films. This work is expected to extend the application of SPMEs by leading to enhanced extraction and to development of *in situ* extraction-detection devices. It will also apply to development of online detectors integrated with onsite extraction systems using ethanol,[6] where extracted compounds are further concentrated on thin films and detected in real time by absorbance or fluorescence.

EXPERIMENTAL

Materials

The PDMS polymer films (monomer molecular weight = 74 g/mol) were made from a high-purity, platinum-catalyzed silicone elastomer kit (manufactured by Dow-Corning for Factor II, Lakeside, AZ, MDX-4-4210). A block copolymer of poly(DMS-styrene) was provided from a private collection of polymer stock from the Polymer Research Institute at the State University of New York, College of Environmental Science and Forestry. This copolymer consisted of dimethylsiloxane with 25% styrene monomers present by mole ratio (average monomer molecule weight = 69.7 g/mol). Acetone, toluene, naphthalene, anthracene, and pyrene (Aldrich Chemical, St. Louis, MO) and dimethyldichlorosilane (Alltech, Fresno, CA) were used. All ethanol/water solvent mixtures were made from high-pressure liquid chromatography (HPLC)-grade ethanol (95 parts ethanol, five parts isopropyl alcohol; Omnisolv, Charlotte, NC), and 18 MΩ cm water prepared with a Millipore Milli-Q Gradient system, Quantum EX model.

Instrumentation

Spin coating was done on a Headway Research (Garland, TX), rotary spin coater (Model #CB15). Chromatographic analysis of ethanol/water fractions was performed on a Agilent 1100 series HPLC with a 100 × 4.6 mm Prodigy 5u ODS(2) reversed phase column (Phenomenex, Torrance, CA), and Agilent Series 1100 Variable Wavelength Detector (G1314A, Santa Clara, CA, Model #G1314A). Naphthalene was detected at 254 nm, anthracene at 365 nm, and pyrene at 334 nm. One microliter of analyte solution was injected per sample. Trials were run for 10 min with an isocratic ethanol solvent at a flow rate of 1 mL/min. The gas chromatography–mass spectrometer was a Hewlett-Packard 5890 Series II with a Phenomonex 2B-5 column (30 m × 0.25 mm i.d. × 0.25 μm). Starting temperature was 70°C for 10 min, increasing at a rate of 10°C/min to 200°C, and held for 15 min. Compounds were detected by mass spectrometer (Hewlett-Packard, Palo Alto, CA, Model # 5972) using single ion monitoring for the molecular ion of each PAH within its retention time window.

Polymer Preparation

Polymer films were prepared on borosilicate glass slides. Densities were 1.01 g/mL for PDMS and 1.05 g/mL for the poly (DMS-styrene) copolymer. Composition of the polymers was confirmed by ^{1}H-NMR. Before mounting the polymer film, slides were cleaned with acetone and baked at 110°C for 3 h. The slides were silated with dimethyldichlorosilane as a 5% by volume solution in toluene. Slides were soaked for 15 min in the solution, rinsed with toluene, and soaked in methanol for 15 min. Slides were weighed before and after coating with polymer to determine the mass of the polymer film.

To create a PDMS film, cross-linking agent was added to the oligomer in a 1 : 10 ratio in a vial, mixed thoroughly with a spatula, and then centrifuged in a test tube for half an hour at 800 rpm to eliminate bubbles. Approximately 10 mL of uncured, liquid polymer was coated onto a preweighed, silated slide. The slide was attached to a rotary spin coater and spun at 500 rpm for 5 min. To cure, the slide was placed in an oven for 3 h at 110°C. Before using, the slide and polymer were cooled to room temperature and reweighed.

Poly(DMS-styrene) copolymer films were similarly prepared. Ten milligrams of copolymer pellets were dissolved in dichloromethane. The copolymer solution was added dropwise to a preweighed, silated slide. These were spun on the rotor at 500 rpm. Not all of the solution remained on the slide through the spinning process. The methylene chloride was removed by evaporation for 3 h in a 75°C oven. Slides were reweighed after coating to determine the mass of polymer applied.

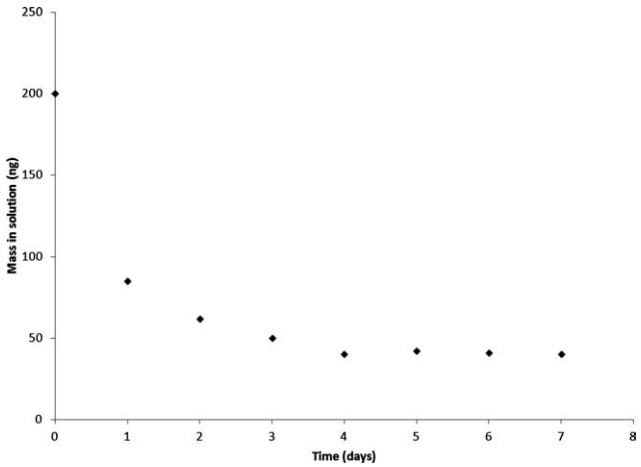

Figure 2. The decrease in mass of pyrene in 70% water/30% ethanol solution over time as ($C_{initial}$ = 0.1 μM) 2-mL PDMS thin film reaches steady state with solution.

Partition Coefficient Determination

PAHs were dissolved in ethanol first, and then added to the aqueous portion of the solvent mixture. Ten milliliters of 0.1 μM PAH solutions and a polymer film-coated slide were placed in a screw cap glass vial with a Teflon-lined septum. Typically, slides were allowed to equilibrate for 7 days. Preliminary trials where a 50 μL aliquot of solution was analyzed daily indicated that this was sufficient time to reach equilibrium (see Results section). After equilibration, the slide was removed from the solvent. The remaining compound in the solvent was extracted with 10 mL of toluene. The compound in the polymer film was extracted by soaking the polymer-coated slide in 10 mL of toluene for 24 h. Both extracts were concentrated to 1 mL under nitrogen gas in a 30°C water bath.

Masses of test compounds present in the ethanol mixtures were determined by HPLC. Masses of test compounds present in toluene extracts were determined by gas chromatography–mass spectrometry (GC–MS). Compounds absorbed onto the polymer-coated glass slides were also determined by optical absorbance.

Partition coefficients (*K*p) were calculated as:

$$K_p = \frac{\text{Moles compound i/volume polymer}}{\text{Moles compound i/volume solvent}} \quad (1)$$

Polymer volume was calculated from the mass of the film and the densities of the polymer.

Standard solutions for instrument calibration were prepared from compounds of known purity (>99% or best available) by weighing on a calibrated analytical balance and dissolving in known solvent volumes with standard laboratory volumetric glassware. Chromatographic analyses were standardized at five concentration levels initially, and response was checked at two or more levels daily when analyses were performed. Detection limits were established at three times the standard deviation of the lowest level standard. Retention time windows for GC–MS and HPLC were established as three times the standard deviation of retention times for standards. Experiments were performed in duplicate. Mass balances were performed on partitioning experiments. Experiments which did not balance within 15% were investigated to determine the cause of the imbalance.

Optical Absorbance

Absorbance as a function of areal concentration was determined for pyrene in the polymer films. Polymer-coated slides were equilibrated with a blank and five known masses of pyrene in a solution of ethanol and water. After equilibration, the mass of pyrene remaining in solution was measured, and the mass absorbed by the polymer was calculated by difference. Areal concentration was calculated as the mass of pyrene absorbed by the polymer divided by the area of the polymer film. Slides were attached to a fixed mounting bracket in the light path of a spectrophotometer (Hewlett Packard 8453) after exposure to pyrene solutions. Absorbance spectra (340–600 nm) were acquired at the center and each corner of a slide, and the absorbance for the five points were averaged. Blank spectra (slides exposed to blank water) were subtracted from spectra for slides exposed to pyrene. After the absorbance experiments, slides were desorbed with toluene and the presence of pyrene was confirmed by GC–MS. However, masses determined by GC–MS were not used for extinction coefficient determinations because of the possibility of loss of pyrene by UV exposure and volatilization during the absorbance experiments.

RESULTS AND DISCUSSION

Controlling Partitioning

PAHs approached equilibrium between the PDMS polymer-coated slide and the solution within 4 days. A representative trial of pyrene with PDMS and 70% water/30% ethanol is shown in Figure 2. This trial yielded a partition coefficient of 21,100. Equilibrium was reached in approximately the same amount of time for all solutions and compounds. In practice, partition coefficients were determined after 7 days to ensure equilibrium.

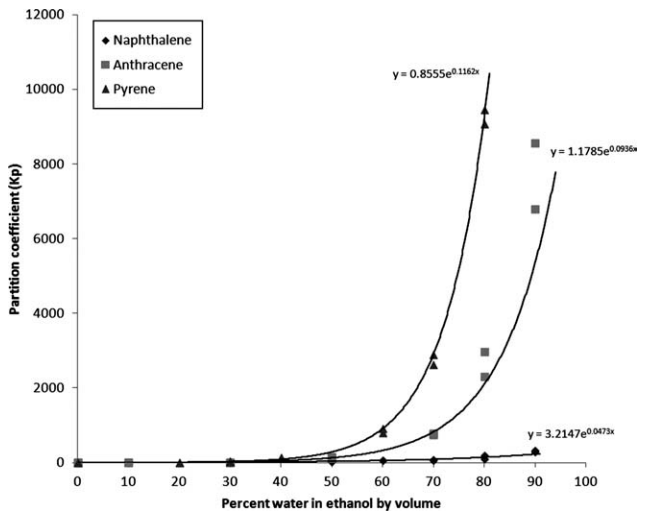

Figure 3. The percent water in ethanol (v/v) versus the partition coefficient on PDMS (◆= naphthalene, ■ = anthracene, ▲ = pyrene).

Table I. Partition Coefficients for Selected Polycyclic Aromatic Hydrocarbons in Water–Ethanol Mixtures to PDMS and Poly(DMS-styrene) Copolymers

	50% Water, average $K_P \pm \sigma$ $n = 2$)		70% Water, average $K_P \pm \sigma$ ($n = 2$)		100% Water, log $K_P \pm$ SE[8]
Compounds (log K_{ow})[9]	PDMS	Poly(DMS-styrene) copolymer	PDMS	Poly(DMS-styrene) copolymer	PDMS
Naphthalene (3.33)	1.45 ± 0.28	2.76 ± 0.07	1.86 ± 0.09	2.99 ± 0.08	2.91
Anthracene (4.68)	2.12 ± 0.05	3.01 ± 0.025	2.88 ± 0.018	3.76 ± 0.011	3.84 ± 0.01 ($n = 44$)
Pyrene (5.13)	2.45[a]	3.99 ± 0.015	3.44 ± 0.03	4.54 ± 0.03	4.32 ± 0.01 ($n = 44$)

[a] Denotes extrapolated values from exponential functions.

Partition coefficients increase exponentially with percent water in ethanol for each of the PAHs tested (Figure 3). This exponential behavior is consistent with solvophobic theory and observation in, for example, reversed-phase liquid. The exponential increase in partitioning is consistent with solvophobic theory. For example, this behavior is the basis for reversed-phase liquid chromatography.[7] We do not observe any swelling of the polymers in any of the solvent mixtures. Therefore, it is likely that the increase in partition coefficients is primarily due to increasing activity coefficients of the hydrophobic solutes in water/ethanol solvents as water is added. Partition coefficients in all solvent mixtures increased in the order naphthalene < anthracene < pyrene, which follows their order of hydrophobicity as indicated by octanol–water partition coefficients (K_{ow}) (Table I). This is also consistent with solvophobic theory, which predicts that larger molecules will partition more strongly to a hydrophobic phase from an aqueous phase.

Partition coefficients to PDMS can be very large in 100% water, approaching 1000 even for naphthalene (Table I). Consequently, PDMS is a useful material for water sampling and is widely used in SPME devices. However, to recover analytes in an ethanol extract, large volumes of water must be added to the ethanol to achieve large partition coefficients. For example, for a given volume of ethanol, 2.3-fold more water is needed to reach 70% water/ethanol than is needed to reach 50%, and fourfold more is needed to reach 80%. This also results in a 1.7-fold increase in dilution factor of the extract from 50 to 70% water, and 2.5-fold increase to 80%. Although partition coefficients increase more rapidly than dilution factors with water addition (Table I), this does reduce the effectiveness of a fixed amount of polymer for recovering compounds from a fixed volume of ethanol. It also creates an operational problem of the amount of pure water that must be supplied to a remote automated system, and it creates increased opportunities for contamination.

This problem may be reduced using a polymer with a greater affinity for the solutes. Table I compares the partition coefficients for PDMS and the poly(DMS-styrene) block copolymer.

Partition coefficients are 10–30-fold higher for the copolymer than for PDMS. Notably, partition coefficients increase more by changing from PDMS to the copolymer at 50% water than by increasing solvent water content from 50 to 70% for PDMS. The improved performance of poly(DMS-styrene) copolymers may be due to the heterogeneous structure[10] of the block copolymer. PS and PDMS have different surface tensions of 19.9[11] and 40.7 mN/m,[12] respectively, so that the siloxane and styrene blocks segregate into different regions within the copolymer matrix. PAHs are likely to absorb and diffuse into the PDMS regions because of their rubbery, less rigid structure.[13] Because of polystyrene's glassy character, PAHs adsorb to the surface of the PS regions[4] rather than diffusing through the matrix, creating high concentrations on the surface of the PS regions. Partitioning to the copolymer is likely driven by solvophobic interactions resulting in partitioning to the hydrophobic polymer as well as by electronic interactions between the aromatic hydrocarbons and the phenyl moieties on the PS. Thus, compounds are both absorbed and adsorbed. Adsorption to the surface of the polystyrene region of the copolymer may create locally higher PAH concentrations.

PDMS is an easily accessible material, relatively easy to work with, inexpensive, and consequently widely used. However, the results above demonstrate that the copolymer has significant advantages as a solid-phase extraction medium for PAHs in water and water/ethanol solution. It also has benefits as a medium for optical detection of extracted compounds. Both exciplex bonds to the phenyl side chain of the polymer and excimer bonds between the same compounds are likely to form when distribution through the polymer is nonuniform. The pyrene absorbance spectrum is red-shifted 4 nm in the copolymer relative to PDMS (Figure 4). This red-shift agreed closely with the 3.5-nm red-shift observed in pyrene–polystyrene interactions observed by Char et al.[4] This indicates the presence of excimers

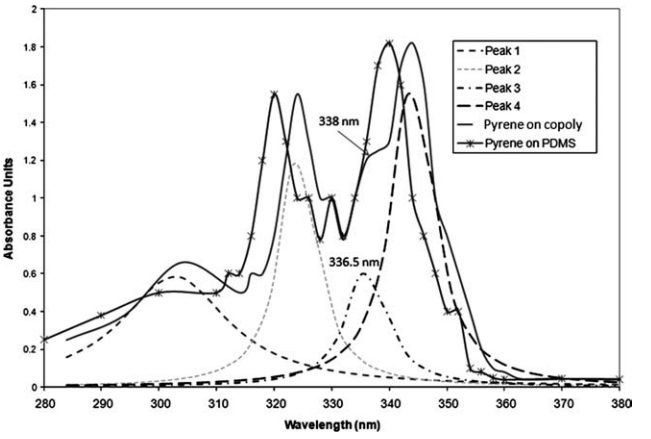

Figure 4. Absorbance spectra for pyrene on PDMS and poly(DMS-styrene) copolymer. Analysis by Lorentz peak fit of pyrene on the copolymer also shown.

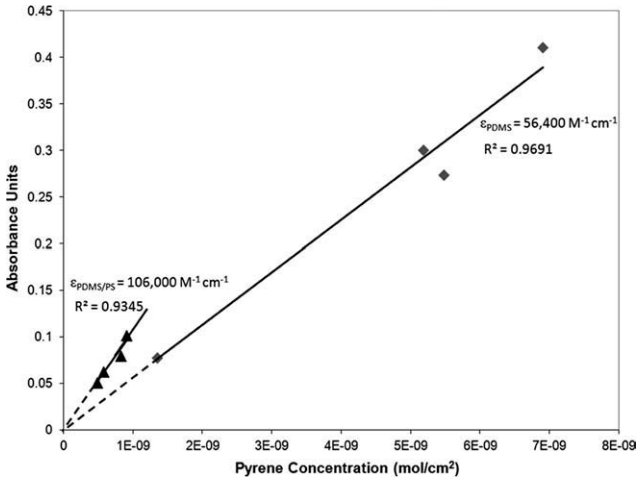

Figure 5. Absorbance (334 nm) versus pyrene concentration per film area (mol/cm^2) for PDMS and poly(DMS-styrene) copolymer films. Extinction coefficients shown are derived from the slope of the linear regression.

or exciplexes for the poly(DMS-styrene) copolymer with absorbed pyrene. Penner et al.[14] have shown that the phenyl side chains on polystyrene and PAHs have strong π–π interactions, so the overlapping π-bonds of the exciplex and excimers are likely to be responsible for the increased partition coefficients relative to PDMS described above.

Figure 4 also shows an analysis by Lorentz peak fit of the copolymer spectrum. This reveals a peak at 336.5 nm with λ_{max} close to the peak at 338 nm in the pyrene/PDMS spectrum. An additional peak (Peak 4) appears at 344 nm. It is likely that Peak 4 is the 339 nm peak in PDMS red-shifted in the copolymer. Peak 3 may represent an interaction of pyrene with PS that does not occur in PDMS.

Both polymer films were evaluated as matrices for optical detection. Figure 5 shows that the absorbance at 334 nm was linear with pyrene mass trapped per unit area of film for both polymers. The relationship between areal concentration and absorbance can be characterized by the extinction coefficient. The extinction coefficient of pyrene in PDMS (56,400 M^{-1} cm^{-1}) is similar to its value in cyclohexane (54,000 M^{-1} cm^{-1}). However, the poly(DMS-styrene) copolymer shows nearly double the response, with an extinction coefficient of 106,000 M^{-1} cm^{-1}, making it a more sensitive tool for optical detection.

The copolymer investigated here has a 10–30× higher affinity for PAHs in water and aqueous ethanol solutions than does PDMS, and trapped pyrene exhibits a twofold greater absorbance response in the copolymer. These results indicate that the copolymer would yield superior performance as an extraction medium and as a detection medium for extracted compounds without further sample processing.

CONCLUSIONS

PDMS and poly(DMS-styrene) copolymers have properties that make them useful as traps and optical detection matrices for hydrophobic organic compounds in water and aqueous ethanol solutions. For both polymers, the degree of partitioning from ethanol solutions could be controlled by addition of water, so that a range of compounds with variable hydrophobicity could be trapped. However, the copolymer has several chemical characteristics that make it the preferred material, at least for polycyclic aromatic compounds. The attractions between these compounds and the phenyl groups on polystyrene block result in a higher partition coefficient for the aromatic compounds pyrene, anthracene, and naphthalene. In addition, pyrene trapped in the copolymer has nearly twice the extinction coefficient as it does in PDMS, providing a more responsive optical matrix for trapped PAHs. The mechanical properties of this polymer are also favorable. After more than 100 assays with different compounds and solvents, neither PDMS nor poly(DMS-styrene) copolymer films delaminated from the glass slide or lost their transparency. PDMS does have the advantage of being commercially available as of this writing, whereas the copolymer was custom synthesized.

We are currently exploring application of both polymers in online extraction/optical detection systems, guided by the results presented in this study, with the goal of capturing fluctuations in water concentrations on a time scale appropriate to environmental monitoring needs. Future work on this system will include manipulating the PDMS to PS ratio to determine the effect on partitioning of hydrophobic compounds and on optical detection of PAHs and other classes of compounds, while maintaining desirable mechanical properties. A simple dip system could also be developed where film-coated slides are exposed to water samples and then placed directly into a spectrophotometer for qualitative and quantitative spectral analysis.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support for this work by Syracuse Center of Excellence CARTI project award, which is supported by a grant from U.S. Environmental Protection Agency [Award No: X-83232501-0]. This work has not been subjected to the Agency's required peer and policy review and, therefore, does not necessarily reflect the views of the agency and no official endorsement shall be inferred. This work was also supported by the Army Research Office under agreement number W911NF-05-1-0556 to the Research Foundation of the State University of New York. The authors also thank Nan Qin for mathematical contributions and Dr. Youxin Yuan for valuable technical assistance.

REFERENCES

1. Ouyang, G.; Pawliszyn, J. *Anal. Bioanal. Chem.* **2006,** *386*, 1059.
2. Bruheim, I.; Liu, X.; Pawliszyn, J. *Anal. Chem.* **2003,** *75*, 1002.
3. Bragg, L.; Qin, Z.; Alaee, M.; Pawliszyn, J. J. *Chromatogr. Sci.* **2006,** *44*, 317.
4. Char, K.; Frank, C. W.; Gast, A. P. *Langmuir* **1989,** *5*, 1335.

5. Toepke, M. W.; Beebe, D. J. *Lab Chip* **2006,** *6*, 1484.
6. Lyons, R. A.; Cole, K. V.; Hassett, J. P. *Appl. Spectrosc.* in review.
7. Horvath, C.; Melander, W. J. *Chromatogr. Sci.* **1977,** *15*, 393.
8. Ter Laak, T. L.; Barendregt, A.; Hermens, J. L. *M. Environ. Sci. Technol.* **2006,** *40*, 2184.
9. Schwarzenbach R. P.; Gschwend P. M.; Imboden, D. M., Eds. Environmental Organic Chemistry, 2nd ed.; Wiley: Hoboken, NJ, **2003.**
10. Andersen, T. H.; Tougaard, S.; Larsen, N. B.; Almdal, K.; Johannsen, I. J. *Electron. Spectrosc. Relat. Phenom.* **2001,** *121*, 93.
11. Okubo, T. J. *Colloid. Interface Sci.* **1995,** 171.
12. Ismail, A. E.; Grest, G. S.; Heine, D. S.; Stevens, M. J. *Macromolecules* **2009,** *42*, 3186.
13. Tamai, Y.; Tanaka, H.; Nakanishi, K. *Macromolecules* **1994,** *27*, 4498.
14. Penner, N.; Nesterenko, P.; Ilyin, M.; Tsyurupa, M.; Davankov, V. *Chromatographia* **1999,** *50*, 611.