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Ultraviolet Photoinitiated On-Fiber Copolymerization of Ionic Liquid Sorbent Coatings for Headspace and Direct Immersion Solid-Phase Microextraction

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ABSTRACT: A high-throughput method for the production of solid-phase microextraction (SPME) sorbent coatings via ultraviolet (UV) photoinitiated copolymerization of ionic liquid (IL) monomers on a fused silica support is described. The copolymerization of monocationic and dicaticionic IL cross-linkers was performed “on-fiber” using UV initiated free radical polymerization. Mixtures composed of various amounts of the IL cross-linker, UV initiator (DAROCUR 1173), and IL monomer were dip-coated onto an etched and derivatized fused silica support and placed in a high-capacity UV reactor. The method requires no organic dispersive solvent and is much more rapid compared to traditional methods in which polymeric ionic liquid (PIL) sorbent coatings are prepared by 2,2′-azobis(2-methylpropionitrile) (AIBN)-initiated polymerization. Two ionic liquid-based cross-linkers, namely, 1,8-di-(3-vinylimidazolium) octane dibromide ([VIM]2C8 2[Br]) and 1,12-di-(3-vinylimidazolium) dodecane dibromide ([VIM]2C12 2[Br]), were copolymerized with an ionic liquid monomer, 1-vinyl-3-hexylimidazolium chloride ([VHIM][Cl]), to produce polar cross-linked PIL-based SPME sorbent coatings. The cross-linking and immobilization of these coatings make them particularly applicable in direct immersion SPME. The coatings were applied in the extraction of polar analytes, including alcohols, aldehydes, and esters, from aqueous solutions using headspace and direct immersion SPME gas chromatography mass spectrometry (GC/MS). Compared to linear PIL-based sorbent coatings containing the same anions, the cross-linked PIL-based coatings exhibited higher thermal stability and lower bleed, making them ideal for GC/MS. Recovery experiments were performed in deionized, well, and river water. The structural integrity of the sorbent coatings, as well as their analytical precision, was not diminished after 90 extractions from complex samples using headspace and direct immersion SPME.

Over the past decade, solid-phase microextraction (SPME) has been a widely adopted extraction method due to its ease of operation, high throughput nature, and significant preconcentration capabilities for a wide range of analytes. SPME is based on the partitioning of analytes to a thin sorbent coating that is coated or immobilized on a fiber support. One main advantage of SPME over other extraction methods is that it combines sampling and sample preparation into one step and does not require complicated instrumentation.1,2 This technique has been successfully applied in food, pharmaceutical, environmental, and even biological analysis using a variety of commercially available as well as laboratory fabricated coatings.3–6 Current interests in SPME are focused toward the development of analyte-selective and stable sorbent materials applicable for complex real-world samples with capabilities to determine analytes at ultratrace levels.7–9 Due to the expansion of SPME into multiple scientific disciplines, the development of new sorbent coating technologies is crucial for the continued longevity and applicability of this technique, particularly when highly selective extractions are desired.

The chemical makeup and composition of sorbent coatings is largely responsible for imparting the unique selectivity observed in SPME and has been a subject of intensive research in recent years.4 Our group has focused on the development of selective SPME sorbent coatings using polymeric ionic liquids (PILs).10 The unique physicochemical properties inherent to ionic liquids (ILs), including high thermal stability, negligible vapor pressure, and tunable solvation capabilities, can be combined with the covalently bonded microstructure of PILs to produce stable SPME sorbent coatings.11 A number of reports have described PIL-based sorbent coatings for the analysis of various classes of target analytes including carbon dioxide,12 polycyclic aromatic hydrocarbons (PAHs),13–17 genotoxic or structurally alerting alkyl halides and aromatics,18 alcohols and amines,19–22 esters and fatty-acid methyl esters (FAMES),23,24 benzene derivatives,25 estrogens,26 and pyrethroids.27 In many of these studies, the PIL-based sorbent coatings were structurally modified and tuned to improve the stability of the coating, enhance its suitability for a specific mode of SPME, and allow it...
to be more selective for a particular class of analyte(s). Such modifications include utilizing the hydrogen bond basic nature of halide anions, substituting aromatic moieties into the IL monomer for enhanced $\pi-\pi$ interactions, and utilizing the numerous hydroxyl within glucaminium-based PILs groups for enhanced hydrogen bonding interactions.

Although PIL-based sorbent coatings possess a number of advantages, there are also limitations. There is currently a lack of neat PIL-based coatings capable of extracting polar analytes, such as alcohols, amines, esters, acids, and aldehydes using direct immersion SPME. This extraction mode is especially important for polar analytes that possess low volatility or exhibit high affinity to the aqueous matrix. All of the previously reported neat polar PIL coatings have been used in headspace extraction due to the susceptibility of the coating sloughing off the fiber when subjected to the aqueous matrix. Recent reports have incorporated sol gel networks containing a PIL to produce thermally and chemically stable coatings. However, the unique selectivity offered by sorbent coatings composed solely of ions (e.g., IL or PIL) may be diminished due to a large percentage of the coating being the silica-based sol. Electrochemical polymerization has also been utilized to load an IL/polyaniline composite onto a substrate to enhance the stability of the coating. However, this technique requires the use of costly materials for the fabrication of the IL-composite fibers. Dicationic IL cross-linkers have recently been utilized in the synthesis of PIL-based sorbent coatings for the headspace extraction of polar analytes. Although this method represents a promising application of IL cross-linkers for PIL-based sorbent coatings, the coating process requires the use of dispersive coating solvents such as dimethyl sulfoxide during synthesis and the need to recoat the PIL to achieve high loading volumes. Analogous to the coating of linear PILs, the organic solvent is needed to facilitate loading of the polymer on the fiber support. However, if solvents are to be used during the coating process, it is imperative that they be sufficiently volatile and be completely removed to prevent elevated background during analysis. An ideal approach would eliminate the need of organic solvents completely while still permitting the production of a robust and stable sorbent coating.

In this study, we report a new method for the synthesis and development of sorbent coatings consisting of cross-linked PIL copolymers composed of chloride and bromide anions which are capable of extracting hydrogen bond acidic analytes by headspace SPME and are also applicable for direct immersion SPME. The PIL coatings, consisting entirely of monocationic IL monomers and dicationic IL cross-linkers, were polymerized “on-fiber” utilizing ultraviolet (UV)-initiated polymerization. In an attempt to stabilize and prevent the sorbent coating from being stripped from the fiber, the support was etched and functionalized to promote copolymerization with the PIL coating. The “on-fiber” polymerization approach eliminates the need for organic solvents in the loading of the monocationic IL monomer/dicationic IL cross-linker on the fiber support. This method enables the high-throughput production of SPME fibers containing cross-linked PIL sorbent coatings, as only one mixture containing a specific composition of the monocationic IL monomer, dicationic IL cross-linker, and initiator is required to dip-coat multiple fibers prior to polymerization in a high capacity UV reactor. This study represents the first report to

Figure 1. Schematic demonstrating the approach used to modify the fused silica support and bond the cross-linked PIL copolymeric sorbent coatings. Scanning electron micrographs were obtained after each step to show the effects of each modification on the surface morphology of the fiber. Insets are shown to provide enhanced morphological detail.
utilize neat cross-linked PIL copolymers containing chloride and bromide anions as sorbent coatings for both headspace and direct immersion studies of polar analytes. A total of 14 sorbent coatings were studied to investigate the effect of cross-linking and initiator content on the ensuing polymerization reaction.

**EXPERIMENTAL SECTION**

**Materials.** 1-Vinylimidazole, 1,8-dibromo-octane, 1,12-dibromo-dodecane, vinyltrimethoxysilane (VTMS), 2,2′-azobis-(2-methylpropionitrile) (AIBN), 1-chlorohexane, ammonium hydrogen difluoride, and 2-hydroxy-2-methylpropiophenone (DAROCUR 1173) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). All analytes examined in this study were purchased from Sigma-Aldrich. Acetonitrile, acetone, chloroform, methanol, n-hexane, isopropanol, dichloromethane, and ethyl acetate were purchased from Fisher Scientific (Fair Lawn, NJ, USA). Ultrapure water (18.2 MΩ/cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Homemade SPME fibers consisting of untreated fused silica capillary tubing (0.5 mm ID) and a 10 μL Hamilton syringe were purchased from Supelco (Bellefonte, PA) and Hamilton (Reno, NV, USA), respectively. Amber glass vials (20 mL) with polytetrafluoroethylene (PTFE)/butyl septa caps were purchased from Supelco. A RPR-100 UV reactor employing a spinning carousel was obtained from Southern New England Ultraviolet Company (Bradford, Connecticut). The UV reactor utilized 16 lamps that produced 254 nm radiation.

**Methods.** The structures of the monocationic and dicatonic IL monomer and cross-linkers are provided in Figure S1 of the Supporting Information. The 1-vinyl-3-dicationic IL monomer and cross-linkers are provided in Table 1. Coating mixtures were prepared by dissolving 15, 30, and 50% (w/w) of the cross-linker in the [VHIM][Cl] IL monomer. The relative to the mass of the [VHIM][Cl] IL monomer. The detailed synthesis procedures, in addition to 1H NMR and electrospray ionization (ESI)-MS spectra, are provided in Supporting Information (Figures S2–S7).

Homemade SPME fibers were prepared according to previous procedures. A series of fiber modification steps, as shown in Figure 1, were employed prior to coating the monomer, cross-linker, and initiator mixture in order to establish a stable film of the sorbent coating on the fiber surface. First, the bare fiber was etched according to a previous method modified by our group. The 1 cm bare silica portion of the fiber was immersed into a methanolic 5% (w/v) ammonium hydrogen difluoride solution for 30 min, air-dried for 30 min, and conditioned in a GC injector at 250 °C for 1 h. The fiber was then washed thoroughly with water to remove excess salt and further conditioned in the GC injector at 250 °C for 5 min. To facilitate the covalent bonding of the cross-linked copolymer matrix to the surface and further enhance the chemical stability of the coating, the etched fiber was immersed into 10 mL of a VTMS solution to incorporate vinyl functionality onto the fiber surface. Characterization of all fiber surfaces and their morphology was performed using a JEOL JSM-7500F scanning electron microscope (SEM).

Mixtures containing varying amounts of monocationic IL monomer, dicatonic IL cross-linker, and initiator were prepared to investigate the thermal properties and the extraction performance of the resulting sorbent coatings. The composition of each copolymer coating prepared and their respective naming system are provided in Table 1. Coating mixtures were prepared by dissolving 15, 30, and 50% (w/w) of the cross-linker in the [VHIM][Cl] IL monomer. The
$[(\text{VHIM})_2]\text{C}_6^2\text{[Br]}$ IL cross-linker exhibited high solubility in the $[\text{VHIM}][\text{Cl}]$ IL monomer and dissolved fully at room temperature by stirring. The $[(\text{VIM})_2\text{C}_6^2\text{[Br]}]/[\text{VHIM}][\text{Cl}]$ IL mixture was heated to 40 °C for 10 min followed by vigorous stirring in order to ensure complete mixing of the two components. Subsequently, 1 or 3% (w/w) of the DAROCUR 1173 UV-initiator was added and stirred, and the coating mixture was evenly applied to the derivatized fiber via dip-coating. The coated fibers were then subjected to UV-initiated free-radical polymerization in a UV reactor at 254 nm for 2 h. Following polymerization, each fiber was exposed to the GC injector at 175 °C for 5 min to monitor bleeding of the sorbent coating. This process was repeated four times for each fiber. Thermal gravimetric analysis (TGA) was used to characterize the IL monomeric mixtures and cross-linked PIL sorbent coatings. Experimental procedures and results for TGA are provided in Supporting Information (Figure S8).

Table S1 (Supporting Information) lists the names and structures for all analytes examined in this study. Working standards were prepared by dissolving each analyte individually in acetonitrile at a concentration of 40 mg mL$^{-1}$. For headspace analysis, a standard stock solution was prepared from the individual stock solutions by combining all analytes at various concentrations and diluting with acetonitrile. A working standard solution with analyte concentrations ranging from 0.01 to 500 μg L$^{-1}$ was prepared by spiking a specific volume of the standard stock solution into a 20 mL amber sampling vial. In the case of headspace sampling, the vial was filled with 15 mL of a 30% NaCl (w/v) aqueous solution. Ex extractions in headspace mode were performed by exposing the fiber to the headspace of the vial capped with a PTFE/butyl self-sealing septa screw cap at room temperature (22 °C). Agitation was performed at 750 rpm using a magnetic stir bar. Following an extraction time of 45 min, the analytes were thermally desorbed by exposing the fiber to the GC injector at 175 °C for 5 min. Direct immersion studies were performed using a different set of analytes (see Table S1, Supporting Information). The sample was prepared by pipetting 20 mL of a water solution to a 20 mL amber sampling vial containing a stir bar with amyl concentrations ranging from 0.001 to 75 μg L$^{-1}$.

Recovery studies were performed using select fiber coatings in four different matrices, namely, deionized water, an aqueous solution containing 30% NaCl (w/v), well water, and river water. The well water was obtained from a residential area in Sylvania, OH (USA) while river water was collected from the Maumee River in Maumee, OH (USA). Preparation of the collected river and well water samples consisted of filtering the samples to remove microscopic particulate matter through a 13 mm syringe filter with 0.45 μm Nylon filter units (Fisher Scientific). The relative recoveries of analytes were evaluated using both SPME sampling modes. Relative recovery was determined by spiking a known concentration of the analyte to a sample solution and comparing the experimental concentration obtained with respect to the actual concentration. Carrying was monitored regularly and was found to be less than 5%.

Evaluation of precision and analytical performance for all fibers was performed using an Agilent 7890 gas chromatograph (Santa Clara, CA, USA) coupled to a 5975C inert XL MSD with a Triple Axis detector (GC/MS). Detection of all analytes via single ion monitoring (SIM) mode was accomplished by monitoring 2 to 3 relevant m/z fragments for each analyte, as shown in Table S1, Supporting Information. Helium was used as a carrier gas with a flow rate of 1 mL min$^{-1}$. All analyses were performed in the splitless injection mode using a CP-Wax 57- CB (50 m × 250 μm × 0.20 μm) column purchased from Agilent Technologies (Palo Alto, CA).

## RESULTS AND DISCUSSION

### Characteristics of Cross-Linked Copolymeric PIL Sorbent Coatings for Headspace and Direct Immersion SPME

The analysis of polar analytes in aqueous sample matrices remains a challenge in SPME. Functionalizing PILs with polar substituents and/or substituents capable of hydrogen bonding can impart higher selectivity to the sorbent coating for these analytes, leading to enhanced sensitivities and lower detection limits. However, these sorbent coatings have been strictly limited to the headspace extraction mode as they are more susceptible to dissolving in the aqueous sample matrix. Thus, polar analytes with low volatility that cannot effectively be salted out are often difficult to extract with current IL/PIL-based coatings.

It is well-known that cross-linkers can strengthen a polymer network often leading to an enhancement in the overall mechanical strength. For most copolymers, increasing the extent of cross-linking also lowers its solubility in most solvents. To exploit the recalcitrant nature of copolymeric PIL-based materials toward dissolving in aqueous solution, a high throughput “on-fiber” polymerization technique was developed. As shown in Figure 1, the monocationic IL monomer is dissolved with the appropriate amount of cross-linker and initiator and coated onto the fiber support prior to UV polymerization. The entire process is performed in air at room temperature and is consolidated to two primary steps, namely, dynamic dip-coating and exposure to UV radiation. Compared to the traditional PIL coating methods, the “on-fiber” polymerization method requires fewer steps in addition to eliminating the need for applied heat, dispersive organic solvents, and an inert N$_2$ atmosphere, which are often required when synthesizing linear PIL-based sorbent coatings using traditional AIBN polymerization methods$^{10,11}$

To stabilize the cross-linked PIL coatings on the fused silica surface, the support was etched using a methanolic 5% (w/v) ammonium hydrogen difluoride solution. The etching of the support allowed for a higher surface area and a more rigid surface morphology, as shown in Figure 1. The surface was then derivatized with VTMS to impart vinyl functionality to the fiber so that the copolymer matrix could be covalently bonded to the support. Immobilization of the cross-linked PIL-based sorbent coating to the silica support hinders the sloughing off of the coating during direct immersion SPME, particularly in well agitated samples. As shown by the SEM image in Figure 1, the sorbent coating remained smooth and intact after UV polymerization. Immersion of the cross-linked PIL sorbent coating in various solvents including chloroform, methylene chloride, dimethyl sulfoxide, and water under high agitation showed no visible loss of coating by optical microscopy.

The thermal stability of sorbent coatings is an important property which must be investigated to determine the appropriate desorption temperature for purposes of maximizing the fiber lifetime. In the case of imidazolium-based ILs possessing halide anions, thermal stability is governed by their susceptibility to undergo nucleophilic substitution at high temperatures$^{19,32}$ Thermal stabilities of the copolymers developed in this study were monitored by thermal gravimetric analysis (TGA). As shown in Figure S8 (Supporting Information).
Information), the TGA curves for copolymers derived from the monocationic [VHIM][Cl] IL containing different amounts of the [(VIM)\textsubscript{2}C\textsubscript{12}]\textsubscript{2}[Br] dicationic IL cross-linker are compared to the linear poly[(VHIM)[Cl]] PIL prepared by AIBN-initiated polymerization containing no cross-linker. The cross-linked PILs produced by UV polymerization exhibited slightly higher stability than the AIBN-initiated PIL sorbent coating. As the extent of cross-linking was increased, the thermal stability also increased. The enhancement in the copolymer thermal stability is the result of adding cross-linkers containing the less thermally labile bromide anion. A noncross-linked UV-initiated poly[(VHIM)[Cl]] PIL coating was also examined, wherein this coating exhibited lower thermal stability compared to its AIBN-initiated counterpart. From a previous study, it was observed that sorbent coatings incorporating the highly hydrogen bond basic chloride anion exhibited the highest selectivity toward many polar analytes, particularly hydrogen bond acids.\textsuperscript{19} In an effort to preserve the selectivity of the sorbent coatings while optimizing their thermal stabilities, dicationic IL cross-linkers containing bromide anions were combined with the monocationic IL monomer containing the chloride anion.

**Optimization of Extraction Time and Salt Concentration.** The addition of kosmotropic salts can decrease the solubility of the analytes in the aqueous matrix and increase their relative concentration in the sample headspace, leading to an increase in extraction efficiency.\textsuperscript{19,33} Figure S9 (Supporting Information) shows the effect of salt concentration (ranging from 0 to 30% NaCl (w/v)) on analyte extraction efficiency using Fiber 12. The extraction efficiency of all analytes dramatically increased with an increase in salt concentration. Many analytes exhibited over an order of magnitude increase in extraction efficiency at 30% NaCl (w/v) compared to when no salt was added; therefore, this concentration was used for all subsequent headspace SPME studies.

The evaluation of new SPME sorbent coatings often requires an extensive investigation into the partitioning behavior of the examined analytes. Sorption-time profiles were generated for Fiber 6 and Fiber 12 (see Table 1) in headspace mode and Fiber 12 in the direct immersion mode. For headspace SPME, the profiles were obtained by exposing the fiber for different time intervals to the headspace of the sample solution containing the selected analytes in a 30% NaCl (w/v) solution at concentrations shown in Table S1, Supporting Information. The sorption time profile for Fiber 6 is shown in Figure S10, Supporting Information. For most analytes, equilibration was achieved at approximately 45 min except for 1-octanol and \(\alpha\)-ethyl benzene methanol in which equilibration was achieved in approximately 60 min. In the case of Fiber 12, shown in Figure S11, Supporting Information, equilibration times were also reached at approximately 45 min for most analytes. Sorption time optimization for direct immersion studies was performed...
by immersing Fiber 12 in a deionized water sample solution at various time intervals with analyte concentrations shown in Table S1, Supporting Information. Most analytes achieved equilibration at approximately 45 min (see Figure S12, Supporting Information). Since most analytes reached equilibrium with the sorbent coating at approximately 45 min for both headspace and direct immersion SPME, this extraction time was chosen for all subsequent studies.

**Copolymeric PIL-Based Sorbent Coatings in Headspace SPME.** To better understand the effects of copolymerizing PIL cross-linkers with the [VHIM][Cl] IL monomer in terms of analytic extraction efficiency, various dicaticionic IL cross-linker and monocationic IL monomer compositions were compared. Figure 2 shows the extraction efficiency of all analytes for the fourteen different fibers prepared in this study.

![Graph showing extraction efficiency of analytes for different fibers](image)

![Graph showing comparison of extraction efficiency of selected fibers](image)

<table>
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<th>analyte</th>
<th>linear range (μg L⁻¹)</th>
<th>slope ± SDa</th>
<th>LOD (μg L⁻¹)</th>
<th>R</th>
<th>% RSDb</th>
<th>linear range (μg L⁻¹)</th>
<th>slope ± SD</th>
<th>LOD (μg L⁻¹)</th>
<th>R</th>
<th>% RSDb</th>
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Fiber 10

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<td>5.4</td>
<td>1–500</td>
<td>133500 ± 496</td>
<td>0.5</td>
<td>0.999</td>
<td>2.8</td>
</tr>
<tr>
<td>furfuryl pentanoate</td>
<td>0.1–500</td>
<td>951600 ± 8720</td>
<td>0.01</td>
<td>0.999</td>
<td>10.5</td>
<td>0.1–500</td>
<td>1399000 ± 26200</td>
<td>0.01</td>
<td>0.998</td>
<td>5.6</td>
</tr>
<tr>
<td>α-ethyl benzenemethanol</td>
<td>0.1–500</td>
<td>211100 ± 1760</td>
<td>0.01</td>
<td>0.999</td>
<td>4.5</td>
<td>0.1–500</td>
<td>328900 ± 2860</td>
<td>0.01</td>
<td>0.999</td>
<td>5.5</td>
</tr>
</tbody>
</table>

aSD: Error of the slope for n = 7. bDetermined by performing repeated experiments at 50 μg L⁻¹ (n = 3) using an extraction time of 45 min.

Table 2. Figures of Merit of Selected Fibers Using Headspace SPME GC/MS at Room Temperature

![Graph showing comparison of selected fibers](image)

![Graph showing extraction efficiency of analytes](image)

![Graph showing comparison of fiber coatings](image)
linker, outperformed Fiber 6, for all analytes especially 1-octanol, in which 3-fold higher peak areas were observed.

**Analytical Performance of Cross-Linked Copolymeric PIL Sorbent Coatings Using Headspace SPME.** To evaluate the selectivity and sensitivity of the cross-linked PIL coatings, calibration curves were constructed for six representative fibers, namely, Fibers AIBN, UV, 4, 6, 10, and 12. These coatings were selected to investigate the effect of cross-linker added in the copolymer on overall analytical performance. All coatings chosen were produced using 3% (w/w) initiator, as it was observed that many of these coatings produced higher extraction efficiencies compared to copolymers made using 1% initiator. Calibration curves were generated by decreasing the analyte concentration from 500 to 0.1 µg L⁻¹ using a minimum of seven calibration levels. Headspace extractions were performed from an aqueous solution containing 30% (w/v) NaCl at room temperature with an extraction time of 45 min under agitation.

Table 2 lists the figures of merit for the four cross-linked PIL coatings. When comparing the sensitivity of the [(VIM)₂C₆]₂[Br] cross-linked coatings, Fiber 4, which consists of 30% (w/w) cross-linker, exhibited higher slopes for all analytes compared to the higher cross-linked Fiber 6. This observation is especially true for 1-octanol, furfuryl pentanoate, and ethyl hexanoate. The LODs of both fibers ranged from 0.01 to 2.5 µg L⁻¹. The precision, determined by performing triplicate extractions at 50 µg L⁻¹, ranged from 1.0 to 7.0% and 2.1 to 8.4% for Fiber 4 and Fiber 6, respectively. In the case of the two PIL-based coatings containing the [(VIM)₂C₁₂]₂[Br] IL cross-linker, an increase in the extent of cross-linking (from 30% to 50% w/w cross-linker) resulted in an increase in sensitivity for all analytes. The LOD of many analytes using Fiber 12, containing 50% (w/w) cross-linker, were lower than or equal to those of Fiber 10, except for furfuryl propionate. The LODs ranged from 0.01 to 2.5 µg L⁻¹ and 0.01 to 0.5 µg L⁻¹ for Fiber 10 and Fiber 12, respectively.

Calibration studies were also performed using Fiber AIBN and UV in order to study the effects of linear (i.e., non-cross-linked) coatings on sensitivity and precision. As shown in Table S2 (Supporting Information), Fiber AIBN exhibited higher sensitivity for all studied analytes in comparison to Fiber UV. The LOD of Fiber UV was observed to be lower for some analytes due to higher sorbent coating bleed for Fiber AIBN. This resulted in an elevated background and a higher detection limit. The overall LODs ranged from 0.01 to 2.5 µg L⁻¹ for both fibers with precision ranging from 2.1 to 13.3% and 1.1 to 12.0% for Fibers AIBN and UV, respectively.

**Direct Immersion SPME Using Cross-Linked PIL-Based Sorbent Coatings.** Direct immersion SPME in aqueous solutions requires the use of coatings that exhibit extremely low solubility in water. In this study, Fibers 10 and 12, which contained the more hydrophobic [(VIM)₂C₆]₂[Br] cross-linker, were selected to explore the feasibility of the cross-linked PIL sorbent coatings. To examine the sorbent coatings for direct immersion SPME, polar analytes possessing low volatility were chosen as targets, as shown in Table S1, Supporting Information. Calibration curves were obtained by decreasing analyte concentrations from 75 to 0.01 µg L⁻¹ while using a minimum of seven calibration levels. Direct immersion extractions were performed in deionized water at room temperature with an extraction time of 45 min under agitation. Table 3 lists the figures of merit for the extraction of these analytes using the two coatings. The precision of both fibers remained acceptable, even after multiple extraction and desorption steps, ranging from 2.9 to 6.7% and 3.1 to 9.4% for Fibers 10 and 12, respectively. The sensitivity of all analytes was greater for Fiber 12 compared to its lower cross-linked counterpart, which correlates well with previous headspace extraction data. The LODs ranged from 0.001 to 0.1 µg L⁻¹ and 0.001 to 0.5 µg L⁻¹ for Fibers 10 and 12, respectively.

The performance of Fiber AIBN and Fiber UV (employing no cross-linkers) was also compared. In the case of Fiber AIBN, the coating dissolved almost immediately after being immersed into the sample solution; therefore, it was not suitable for direct immersion SPME. On the other hand, Fiber UV remained visibly intact within the matrix. However, an extensive calibration study was not pursued using this coating since the precision was poor (up to 57.8% RSD, data not shown), presumably due to a gradual loss of coating during each extraction/desorption step.

**Method Validation and Recovery.** Recovery experiments were performed to evaluate the applicability of the new generation cross-linked PIL sorbent coatings. Table S3 (Supporting Information) lists the percent relative recovery of the polar analytes in the different water matrices, all of which contained 30% (w/v) NaCl, using headspace SPME. The experiments were performed by spiking 5 µg L⁻¹ of analyte into the selected water matrix and exposing the coating to the sample solution for 45 min under agitation. Blank extractions of the sample matrices were performed to ensure no analyte was present prior to analysis. Fibers 6 and 12 were selected as representative coatings for headspace recovery experiments. The percent relative recoveries using deionized water containing 30% (w/v) NaCl ranged from 78.1 ± 6.4% to 119.1 ± 12.6% and 87.8 ± 3.5% to 119.0 ± 12.1% for Fibers 6 and 12, respectively. Fiber 12 was subjected to further examination using more complex sample solutions. Recoveries ranging from 66.3 ± 10.7% to 109.6 ± 4.2% and 74.1 ± 3.2% to 164.7 ± 8.0% were obtained when examining well and river
water, respectively. The poor recovery for a few analytes can be attributed to the high complexity of the river water matrix.

To further demonstrate the usefulness of the cross-linked PIL coatings developed in this study for direct immersion SPME from real-world samples, Fiber 12 was chosen for the analysis of select analytes from deionized, well, and river water. The experiments were performed by spiking 2.5 \( \mu \text{g L}^{-1} \) of analyte into the water sample and immersing the coating into the sample solution for 45 min under agitation. As shown in Table 4, the relative recoveries ranged from 88.9 ± 2.0 to 112.5 ± 10.3% for deionized water, 70.9 ± 3.2 to 116.0 ± 11.2% for well water, and 58.0 ± 4.1 to 135.8 ± 13.8% for river water, respectively. The poor recovery for a few analytes can be attributed to the high complexity of the river water matrix.

Table 4. Recovery of All Analytes Using Direct Immersion SPME GC/MS for Selected Sorbent Coatings \((n = 3)^{a}\)

<table>
<thead>
<tr>
<th>analyte</th>
<th>deionized water</th>
<th>well water</th>
<th>river water</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-octanol</td>
<td>108.2 ± 8.1</td>
<td>58.0 ± 4.1</td>
<td>105.3 ± 9.9</td>
</tr>
<tr>
<td>fururyl pentanoate</td>
<td>98.7 ± 6.1</td>
<td>101.0 ± 9.1</td>
<td>71.5 ± 1.3</td>
</tr>
<tr>
<td>naphthalene</td>
<td>95.0 ± 7.3</td>
<td>88.0 ± 5.0</td>
<td>70.9 ± 3.2</td>
</tr>
<tr>
<td>(\alpha)-ethyl benzenemethanol</td>
<td>88.9 ± 2.0</td>
<td>116.0 ± 11.2</td>
<td>120.3 ± 7.7</td>
</tr>
<tr>
<td>phenol</td>
<td>112.5 ± 10.3</td>
<td>108.5 ± 16.6</td>
<td>135.8 ± 13.8</td>
</tr>
</tbody>
</table>

*A 2.5 \( \mu \text{g L}^{-1} \) analyte concentration was used for all studies.

\(\approx\) 10.3% for deionized water. The relative recoveries for well and river water ranged from 88.9 ± 2.0 to 112.5 ± 11.2% and 70.9 ± 3.2 to 135.8 ± 13.8%, respectively. These recoveries are very good considering that the river sample was extremely complex and suspended material that could not easily be filtered from the sample was still observed. The sorbent coating was capable of withstanding the complex matrix environment to extract analytes at trace-level concentrations, further demonstrating the durability and stability of the cross-linked PIL-based sorbent coatings for direct immersion studies.

Fiber Lifetime and Integrity. All fibers within this study were sacrificed for analysis via SEM to analyze the coating morphology and determine the approximate film thickness. Scanning electron micrographs of a representative group of coatings are shown in Figures 3 and S13, Supporting Information. Even after multiple extraction and desorption steps, the coatings used for headspace analysis (Figures 3A and S13A, Supporting Information) remained smooth and intact. For the coatings applied in direct immersion studies, (Figures 3B and S13B, Supporting Information), a rougher surface morphology was observed. The rigid surface was highly pronounced for Fiber 12, which was immersed into all three water samples for a total of approximately 90 extraction and desorption steps. It is likely that particulate matter within the complex sample matrix may have affected the morphology of this fiber, particularly true since the only sample preparation performed on the river water sample was to filter particulate matter through a syringe filter. Nevertheless, no discernible loss in analyte extraction efficiency or precision was observed for this fiber coating up until the time that it was sacrificed for imaging purposes.

\[\text{CONCLUSIONS}\]

In over 20 years, SPME has become a very important analytical tool that has married sample preparation and chemical separations. Expanding the types of sorbent coatings to allow for highly selective extractions will continue to expand SPME into new areas of research. The “on-fiber” polymerization approach presented in this study is highly applicable for the high-throughput loading of IL monomers/cross-linkers and synthesis of cross-linked PIL copolymeric sorbent coatings without the need for organic solvents. The etching and derivatization of the fiber support produces a covalently linked and mechanically stable coating capable of enduring high shear forces that result from well-agitated sample solutions. Compared to the linear PIL-based sorbent coatings prepared using AIBN-initiated polymerization, many of the cross-linked PIL-based coatings examined in this study exhibited lower bleed, lower backgrounds, and lower limits of detection. The versatile copolymerization approach described in this study can be easily expanded to IL monomers/cross-linkers with varied chemical structures and cation/anion combinations.

\[\text{ASSOCIATED CONTENT}\]

\[\text{Supporting Information}\]

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.
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Notes
The authors declare no competing financial interest.

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