# Curable Ionic Liquid Prepolymer-Based Ion Gel Coating System for Toxic Industrial Chemical Hazard Mitigation on Porous Substrates

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S *Supporting Information*

ABSTRACT: A peelable gel coating based on a curable ammonium-alcohol ionic liquid (IL) prepolymer has been developed for the decontamination of toxic industrial chemicals (TICs) from porous substrates. The physical properties of these coatings can be tuned by controlling the prepolymer molecular weight (prepared by RAFT polymerization) and by altering the formulation of the initial coating mixture. The initially applied (uncured) solutions can be applied onto porous wood and ceramic substrates with minimal soak-in, and these films cure quickly in situ under ambient conditions. These coatings were tested in a series of assays meant to demonstrate their effectiveness as TIC vapor barriers and materials that absorb liquid TICs from the aforementioned substrates. The coatings were found to suppress ~80% of the vapor released by a TIC simulant (*o*-dichlorobenzene) from these substrates and to extract up to 85% of the mass of the originally applied simulant that soaked into these substrates.
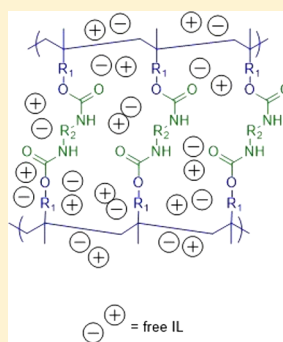
1. INTRODUCTION

A major challenge facing the chemical industry involves the large-scale production and use of toxic industrial chemicals (TICs). The health effects of TICs vary among different compounds, but in general TICs can be classified as carcinogens, neurotoxins, and reproductive hazards.[1−3] In addition, many TICs are nonbiodegradable and can persist for long periods of time following their accidental release into the environment. One pathway by which TICs may persist in the environment is their uptake into a variety of different building or infrastructure materials (e.g., steel, rubber, paint, wood, concrete), which would allow their gradual, continuous diffusion into the nearby air over time.[4−6] This type of slow release of TIC vapors poses a serious health problem for both civilians and first responders to sites of TIC spills.

Currently established TIC capture and decontamination methods include the use of activated charcoal as an adsorbent.[7] TICs can also be exposed to chemical reagents that can chemically degrade the TICs into less harmful products.[1,8,9] However, many TICs are insufficiently adsorbed by activated charcoal, especially those soaked into more complex substrates, and the TIC decontamination reagents are often corrosive and difficult to work with. Current research has also investigated using metal−organic frameworks (MOFs) and palladium nanoparticle catalysts for selective capture and degradation of TICs, but these technologies have yet to be adapted to large-scale use.[10,11] For the removal of TICs trapped in building/ infrastructure materials, heat or hot blown air has been used to increase the vapor pressure of the TICs and extrude them from

the substrate surface (i.e., thermal stripping).[12] However, this method has been observed to be effective for TICs removal only from the upper layers of contaminated substrates, and the released TIC vapors would subsequently have to be captured from the surrounding air.

Ionic liquids (ILs, molten organic salts at ≤100 °C and ambient pressure) have been investigated for TICs mitigation due to their unique combination of properties that make it ideal for this application (i.e., ILs are effectively nonvolatile, have good uptake capability for hydrophobic organic compounds, and are structure- and property-tunable).[13,14] Prior work in this area has included the formulation of a physically gelled IL system using an imidazolium-based IL and a low-molecular-weight organic gelator (LMOG). This physically gelled IL coating system has been demonstrated to be effective for capping the release of TIC simulant vapors and absorbing soaked-in liquid TIC simulants from several contaminated substrates types including painted steel, rubber, glass, and wood.[15] This initial IL-based TIC mitigation coating system was recently improved upon by incorporating step-growth, IL-based poly(alcohol) monomers that could be cured in situ with a commercial di-isocyanate monomer in the presence of free IL to form covalently cross-linked poly(ionic
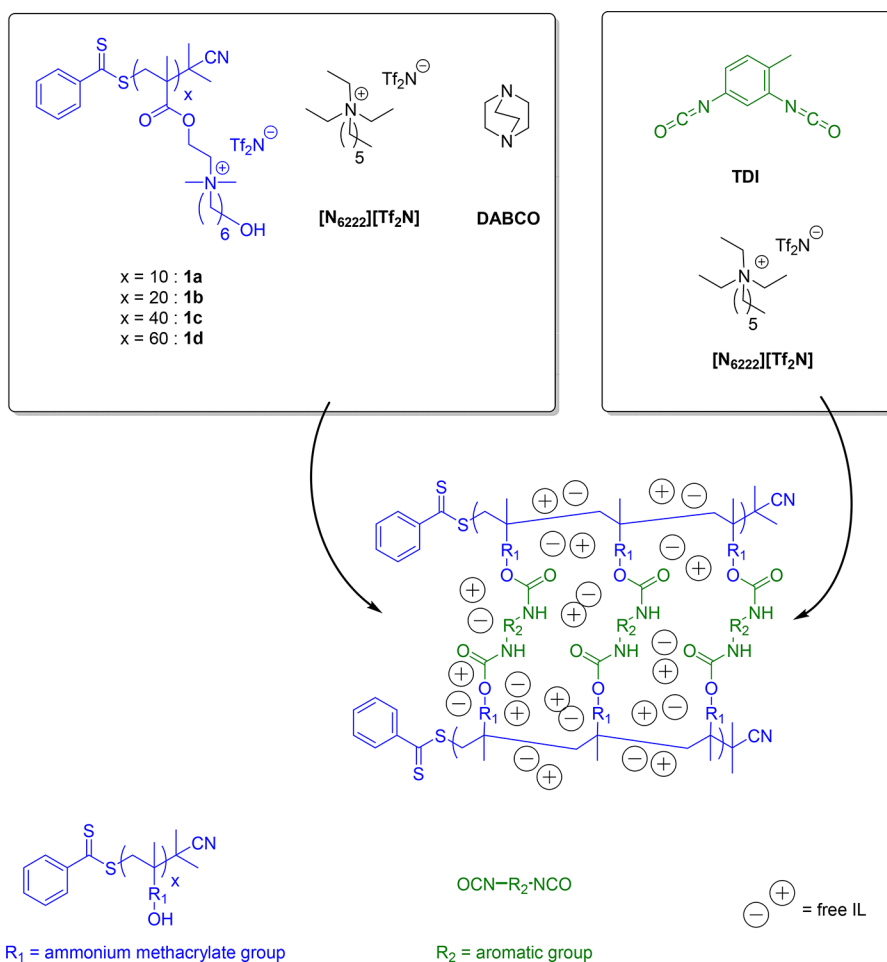
Scheme 1. Structures of Curable Coating Components and Resulting Cross-Linked Polyurethane Network Composite Coatings

liquid) (i.e., PIL)/IL gels, rather than a physical gel.[16,17] In these new curable IL monomer/di-isocyanate monomer/IL coating systems, the added free IL acts as (1) a nonvolatile solvent for the polymerization/curing reaction, (2) as a plasticizer in the cured film, and (3) as a lubricant/release agent that allows facile removal of the cured film from the substrate surface.[18−20] The resulting mechanically robust but flexible, polyurethane-based PIL/IL composite network not only caps the release of TIC simulant vapor and sorbs soaked-in TIC simulant from the contaminated substrate as it cures, but also the final cured film could be easily peeled off the substrate (with minimum substrate surface damage) after application.[16,17]

However, it was observed that the initial mixtures of these curable IL monomer/di-isocyanate monomer/IL coating systems rapidly soaked-into (and sometimes completely through) the more porous substrates tested (e.g., wood, ceramics), thereby removing the ability to remove the cured coating from the substrate.[16,17] This undesired behavior was primarily due to the low viscosity of the initial monomers/IL solution, which contained only low-molecular-weight molecules prior to curing. As a result, the small-molecule-based monomers/IL system could not be applied to highly porous substrates and surfaces. The alcohol-IL monomer/di-isocyanate monomer/IL-based curable system also suffered from slow curing times to reach the gel point, which may have contributed to the low viscosity of the initial mixture.

Additionally, while this initial IL monomer/di-isocyanate monomer/IL coating was effective as a vapor cap for the TIC-simulant-contaminated substrates, the liquid TIC simulant extraction capability of this coating system needed improvement.[17]

Herein, we describe a new curable and peelable IL-based coating system prepared from a controlled-molecular-weight ammonium-alcohol PIL prepolymer (1a−d), toluene di-isocyanate (TDI), a small amount of polymerization catalyst (1,4-diazabicyclo[2.2.2]octane, DABCO), and free IL [N₆₂₂₂]-[Tf₂N] (Scheme 1). This new prepolymer-based IL gel coating system is also based on alcohol-isocyanate step-growth polymer chemistry but minimizes initial coating soak-in on highly porous substrates such as wood and ceramic (due to its higher solution viscosity) and allows facile peel-off of the final cured film.[21−25] In addition, this new curable PIL-based coating system cures faster than the prior small-monomer-based coatings, and its TIC simulant liquid extraction and vapor suppression capabilities are equal to or better than the prior systems. One further benefit of this new curable coating system over the previous IL-monomer-based coating system is the use of less di-isocyanate monomer (which is highly toxic and reactive to water) needed to fully cure the system.

2. EXPERIMENTAL SECTION

2.1. Instrumentation. ^{1}H NMR spectra were obtained using either DMSO-d_6 (for the Br$^-$- and Tf$_2$N$^-$-containing ILs and IL monomers) or acetonitrile-d_3 (for the Tf$_2$N$^-$-containing prepolymers) as the NMR solvents. ^{1}H NMR spectra were acquired using a Bruker Avance-III 300 MHz NMR spectrometer for small molecule characterization and a Varian Inova 500 MHz NMR spectrometer for prepolymer characterization. FT-IR measurements were performed using a Thermo Scientific Nicolet 6700 spectrometer and with salt plates purchased from International Crystal Laboratories. Film and substrate thicknesses were measured using a Cen-Tech digital thickness gauge at three different locations on the sample and averaged. Thermomechanical property measurements were performed using a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA). Gas chromatography–mass spectrometry (GC–MS) measurements were performed using a Thermo-Finnigan ISQ GC–MS system with a column containing a stationary phase of 5% phenyl and 95% methyl polysiloxane. GC–MS analyses were performed over a temperature range of 150 to 280 °C. Scanning electron microscopy (SEM) images were acquired using a JEOL JSM-6480LV scanning electron microscope.

2.2. Materials. 2-(Dimethylamino)ethyl methacrylate, n-bromohexane, and 1,4-diazabicyclo[2.2.2]octane (DABCO) were received from Sigma-Aldrich and used without further purification. 6-Bromo-1-hexanol was synthesized according to a previous procedure.[26] Butylated hydroxytoluene (BHT) was purchased from Sigma-Aldrich and recrystallized from hexanes. Triethylamine (TEA) was received from Sigma-Aldrich and distilled from KOH that was purchased from Fisher Scientific. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was received from Sigma-Aldrich and recrystallized from methanol. Toluene di-isocyanate (TDI) and 10-bromo-1-decanol were purchased from TCI America. TDI was purified via vacuum distillation and stored under dry argon before use. RAFT chain-transfer agent (CTA) 2-cyano-2-propylbenzodithioate was received from Strem Chemicals. Lithium bistrifluorosulfonimide (LiTf$_2$N) salt was purchased from the 3 M Company. Acetonitrile and chloroform solvents were vacuum-transferred over calcium hydride before use. All other solvents were used as received. Wood test substrate samples were cut from 0.625-in. diameter poplar tree dowel samples (Madison Mill Wood Poplar Dowel, purchased from Lowe's) into ∼2 mm-thick discs. Ceramic test substrates were cut from a 4.25 × 4.25 in^2 square unfinished ceramic bisque tile units (purchased from Ceramicartspace.com) into 1 cm^2 samples that were then boiled in water for 1 h after cutting and subsequently dried overnight in vacuo at 100 °C before use. I-Chem septa jars (125 mL capacity) and Al foil cups were purchased from VWR Scientific.

2.3. Synthesis of [N$_{6222}$][Br] and [N$_{6222}$][Tf$_2$N]. The compounds were synthesized according to literature procedures.[27] Characterization data matched those reported for these compounds.[27]

2.4. Synthesis of Compound 2. Synthesized according to literature procedures[28] with modifications: 2-dimethylaminoethyl methacrylate (3.61 mL, 21.4 mmol), 6-bromo-1-hexanol (2.80 mL, 21.4 mmol), BHT, and distilled chloroform (18 mL) were mixed under inert atmosphere in a flask charged with a stir bar. The mixture was heated at 45 °C with stirring for 24 h. The solvent was immediately removed under vacuum.

The bromide product was recrystallized in acetone and ether as a white solid. Yield: 3.12 g (43%). Characterization data matched those reported for this compound.[28]

2.5. Synthesis of Compound 3. Compound **2** (8.71 g, 25.7 mmol) was dissolved in deionized H$_2$O (20 mL), and LiTf$_2$N (7.76 g, 27.0 mmol) was then added to the mixture and allowed to stir overnight at ambient temperature. The formed crude product was extracted with dichloromethane (3 × 20 mL), and the organic layer was washed with H$_2$O (4 × 20 mL). An aliquot of each wash was isolated, and to each aliquot was added two drops of 0.68% aq. HNO$_3$ and three drops of 1 M aq. silver nitrate solution. No further washes were performed once the silver nitrate test did not yield AgBr precipitate. The organic solvent was then removed under vacuum to yield the desired Tf$_2$N$^-$ salt monomer **3** as a clear viscous liquid. Yield: 11.20 g (81%). ^{1}H NMR (300 MHz, DMSO) δ (ppm) 6.08 (s, 1H on alkene), 5.76 (s, 1H on alkene), 4.52 (t, 2H on alkyl), 4.35 (t, 1H on OH), 3.68 (2H on alkyl), 3.38 (4H on alkyl), 3.08 (6H on alkyl), 1.91 (3H on alkyl), 1.67 (2H on alkyl), 1.43 (2H on alkyl), 1.30 (4H on alkyl). ^{13}C NMR (75 MHz, DMSO) δ (ppm) 165.87, 135.37, 126.54, 121.60, 63.92, 61.73, 60.46, 58.09, 50.53, 32.17, 25.65, 25.01, 21.78, 17.84. HRMS (ESI$^+$) calcd for [C$_{15}$H$_{34}$NO$_2^+$], 258.2069; found, 258.2075. HRMS (ESI$^-$) calcd as [Tf$_2$N$^-$], 279.9173; found, 279.9174. Since ILs are known to have combustion issues for elemental analysis,[29] the ^{1}H and ^{13}C NMR spectra and ESI-HRMS spectra for the isolated compound are provided in the Supporting Information to help confirm its purity in lieu of elemental analysis data.

2.6. RAFT Polymerization of Prepolymers 1a–d. All RAFT polymers prepared from monomer **3** were prepared under the following conditions: A 1 M solution of monomer **3** was prepared in distilled acetonitrile. The appropriate amount of chain-transfer agent (CTA) 2-cyano-2-propyl benzodithioate and thermal initiator AIBN was added to synthesize a prepolymer of a specific length X, such that the molar ratio of (**3**: CTA: AIBN) was (X: 1:0.1). The solution was added to a Schlenk flask under an inert argon atmosphere and freeze–pump–thawed three times. The solution was allowed to stir for 24 h at 70 °C. The acetonitrile was removed under vacuum, and end-group analysis via ^{1}H NMR spectroscopy was performed on the crude product to confirm that the correctly sized prepolymer had been made.[30] After confirmation, the prepolymer was purified by precipitation from acetonitrile and ether.

2.7. Formulation of Curable Coatings. The coatings were prepared and applied using a two-solution method described in our previous publication.[17] In general, two precursor solutions denoted A and B were prepared. Solution A contained the hydroxyl-group-containing IL prepolymer (**1a, b, c,** or **d**), 0.01 molar equiv of the DABCO catalyst relative to the moles of TDI, 75% of the mass of the free IL [N$_{6222}$][Tf$_2$N], and ∼1 mL of acetone as a cosolvent. Solution B contained the TDI di-isocyanate monomer and the remaining mass of [N$_{6222}$][Tf$_2$N] . The acetone was removed from Solution A using rotary evaporation, and each solution was then degassed under high dynamic vacuum (ca. 10 mtorr) for 1 h at ambient temperature. Solution A was heated at 70 °C during this time to aid in the removal of the acetone cosolvent, and Solution B was degassed at ambient temperature. The A and B solutions were then combined using a pipet, vortexed briefly, mixed by hand, and applied via spatula to a test substrate.

Scheme 2. (a) Synthesis of Ammonium IL Monomer 3 and (b) RAFT Polymerization of 3 To Form New Step-Growth-Curable IL Prepolymers 1a–d

(a)

(b)

x = 10 (**1a**)
x = 20 (**1b**)
x = 40 (**1c**)
x = 60 (**1d**)
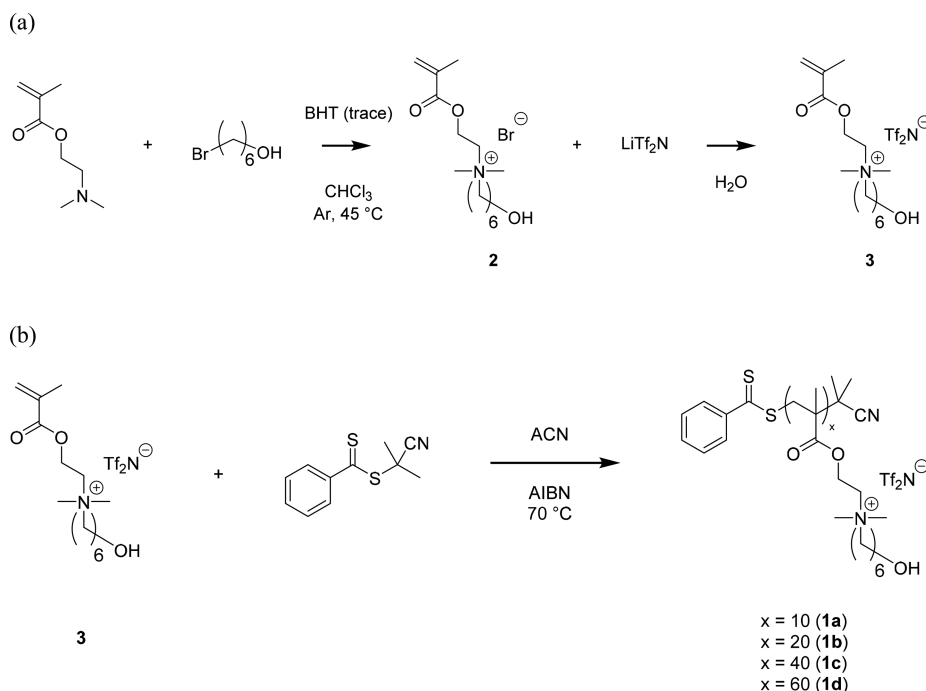
2.8. Curing Kinetics Testing. Samples for FT-IR analysis were prepared according to the two-solution method described above. Appropriate amounts of solutions A and B containing stoichiometrically equivalent amounts of hydroxyl groups from the IL prepolymer and isocyanate groups from the TDI were added to two different NaCl plates, pressed together and rotated several times, and inserted into the FT-IR instrument. The area of the N=C stretching band (absorbance mode) from 2220–2330 cm^{-1} was measured to monitor the disappearance of the isocyanate peak during the reaction, and the peak from 1764–1692 cm^{-1} was measured as an internal reference, since this peak was empirically determined to not change in intensity during polyurethane formation. The reaction was deemed complete when the step-growth polymerization reached its gel point, defined here as the point at which an immobile (i.e., nonflowable) polymer mixture is formed. Mathematically, the gel point was estimated by using a modified version of the Carothers equation and was calculated independently for each prepolymer blend.[31] In general, mixtures were considered fully cured at ~52% disappearance of the isocyanate peak.

2.9. Preparation of Free-Standing Cured Films. The free-standing films were prepared according to the two-solution method described above. In general, films were prepared by combining appropriate amounts of solutions A and B (containing equimolar amounts of hydroxyl group and isocyanate groups, respectively) in a single vial at ambient conditions, vortexing the mixtures for ~3 s, and then transferring the mixtures via pipet onto 25 mm × 25 mm glass slides treated with Rain-X. The polymerization mixtures were then placed in a vacuum chamber under Ar and allowed to cure for 24 h at ambient temperature. The films were determined to be fully cured when they could be removed from the glass slide with a razorblade without the formation of defects. After removal from the glass substrate, the free-standing resulting film was checked by ATR-FT-IR spectros-

copy to confirm degree of polymerization and then analyzed for its mechanical properties.

2.10. Mechanical Properties Testing. The cured free-standing films were cut into ~1 mm-thick rectangular strips, and their dimensions were recorded. The films were inserted into the DMA instrument using a two-point tension clamp system and held isothermally at 30 °C for 5 min. The stress–strain experiments were set up with a preload force of 0.0001 N, a force ramp of 0.3 N/min, and an upper force limit of 10.0 N. The films were monitored by DMA until they fractured.

2.11. TIC Simulant Vapor Headspace Assay. A curable coating mixture was prepared via the two-solution method described above. *o*-DCB (*ortho*-dichlorobenzene, a simulant for polychlorinated biphenyls)[32] was applied to either a wood or ceramic substrate and allowed to equilibrate for 1 min in a screw-top septa jar (setup shown in Figure S2 in the Supporting Information). The coating mixture was then mixed briefly and immediately applied to the substrate. The film was allowed to cure for 24 h, and a glass syringe was used to take a 5 μL sample of the headspace above the film. GC–MS analysis indicated a peak corresponding to the *o*-DCB with a retention time of 2.1 min, and the integration under this peak was compared to an identical GC analysis of the headspace of an uncoated sample.

2.12. Liquid TIC Simulant Extraction Assay. Following the *o*-DCB vapor headspace test, the cured coating was carefully lifted from the substrate using a razorblade. The substrate was then washed with CH$_2$Cl$_2$ three times over the course of 24 h to extract any residual *o*-DCB remaining in the sample. The combined CH$_2$Cl$_2$ washes were diluted 100×, and a 58-ppm-solution of *n*-dodecane in CH$_2$Cl$_2$ was introduced to the combined CH$_2$Cl$_2$ washes as an internal standard. The resulting solution was then analyzed using GC–MS, and the ratio of the *o*-DCB GC peak to that of the internal standard was applied to a calibration curve to determine the number of moles of *o*-DCB extracted by CH$_2$Cl$_2$ from the substrate. The

difference in that number from the original amount of o-DCB applied to the substrate in moles was reported as the amount of o-DCB taken up by the curable IL-based coating.

3. RESULTS AND DISCUSSION

3.1. Selection and Synthesis of New Curable Coating Materials.
Quaternary ammonium ILs and ammonium-alcohol IL monomers have been previously observed to be effective at vapor suppression and uptake of hazardous organic compounds when formulated into polyurethane gels with TDI.[17] Consequently, similar IL starting materials were selected for this study because of their modularity and ease of synthesis and comparison. To generate similar curable coatings but with higher and more controllable initial solution viscosities (to minimize soak-in on porous materials), ammonium-alcohol IL prepolymers of controlled molecular weight and low polydispersity were chosen to replace the original low-molecular-weight IL monomers. To prepare the prepolymer materials, the ammonium-alcohol IL methacrylate monomer **3** was selected due to its inexpensive precursor compound, straightforward synthesis, and its reported success in forming PIL materials in the literature (Scheme 2).[28,33] To prepare the IL prepolymers **1a–d** from **3**, reversible addition–fragmentation chain transfer (RAFT) polymerization was used because of its effectiveness in polymerizing methacrylate monomers and the absence of metal compounds in its chain-transfer agent (Scheme 2). The di-isocyanate monomer, TDI, was selected as the cross-linking agent to form urethane linkages with the ammonium-alcohol IL prepolymers and to serve as a basis of comparison to the previous small-molecule IL monomer method.[17] These components react together to form a cross-linked step-growth polyurethane network, with the advantages of rapid reaction speed, the ability to tune the degree of cross-linking, and a lack of volatile byproducts produced during reaction (which aids in TIC vapor uptake and suppression). $[N_{6222}][Tf_2N]$ was selected as the added free IL in the formulation to increase the plasticity of the final coating and to act as a release agent for the cured film from substrate surfaces. For the complete synthesis details and characterization data for the ammonium IL-based compounds, refer to the Experimental Section and the Supporting Information.

3.2. Curable Coating Formulation.
The coating formulation consisted of prepolymers **1a–d**, TDI, free IL $[N_{6222}][Tf_2N]$, and DABCO as a polymerization catalyst. Prepolymers **1a–d** and TDI were combined in the mass amounts needed to provide the same number of −OH and −NCO groups and allow stoichiometric step-growth polymerization. The total amount of $[N_{6222}][Tf_2N]$ used as the free IL solvent was limited to 57 wt % of the total mass of the initial coating formulation (ca. 980 mg). A lower wt % value of $[N_{6222}][Tf_2N]$ in the formulation resulted in a mixture that cured too quickly to apply to the substrates without significant defect formation, and a higher wt % of $[N_{6222}][Tf_2N]$ was avoided to minimize leaching of $[N_{6222}][Tf_2N]$ from the formed polymer network. The amount of DABCO catalyst used (0.01 molar equiv. relative to TDI; 0.04 wt %) was selected to allow adequate time to apply the initial reactive solution to the test substrates without curing prematurely.

As a control sample, a coating formulation using small-molecule ammonium-triol monomer (10-hydroxydecyl)-bis(2-hydroxyethyl)-methylammonium bis(trifluoromethylsulfonyl)-imide (**4**) was prepared using the conditions described in our previous work.[17] Compound **4** and TDI were combined in a molar ratio of 3:2 in the coating mixture to provide the same number of the −OH and −NCO groups for stoichiometric step-growth polymerization of the coating. The total amount of $[N_{6222}][Tf_2N]$ used as the free IL solvent in this control formulation was limited to a range of 47 wt % of the total mass of the coating, and the total amount of DABCO catalyst was limited to 0.0 wt %. The setup of this control coating was otherwise the same as with the prepolymer-based coatings.

3.3. Initial Coating Mixture Soak-in Testing on Porous Substrates.
As a preliminary test, we wanted to assess to what extent the prepolymer-based coating solutions soaked into porous substrates such as wood and ceramic. This was a major drawback of the previous generation of curable step-growth IL materials, as the small-molecule ammonium-alcohol IL monomers would extensively soak into (and often completely through) wood substrates before curing.[17] We quantitatively determined the amount of soak-in of the prepolymer-based coating mixtures on wood substrates. The coatings containing prepolymers **1a–d** and a control sample containing small-molecule ammonium triol monomer **4** were prepared using the two-solution method described above and were allowed to cure for 24 h in a sealed septa-jar under ambient conditions. As expected, the control coating made from **4** soaked nearly completely into the wood substrate (94 wt % of the originally applied coating was absorbed into the wood). However, the prepolymer-based coatings had significantly less soak-in and were successfully cured and removed as solid films from the surface of the wood (see Figures S15 and S16 in the Supporting Information for photographs). The amount of retention of IL $[N_{6222}][Tf_2N]$ by the coating was related to the chain length of the prepolymer, with prepolymer **1a** having lost 48 wt % of IL $[N_{6222}][Tf_2N]$, while prepolymer **1d** saw only 1 wt % loss of IL $[N_{6222}][Tf_2N]$. The prepolymer-based curable coatings were deemed to be viscous enough to prevent significant soak-through into the porous substrates for this study. See Table 1 for a complete summary of the results.

Table 1. Results of Soak-in Tests Using Porous Wood Substrate[a]

ammonium-alcohol IL prepolymer used in the curable coating mixture	amount of coating mixture soaked into wood (wt % of originally applied mixture)
1a	48
1b	34
1c	34
1d	1
4	94

[a]Films contained prepolymers **1a–d** and TDI in the mass amounts needed to provide the same number of −OH and −NCO groups, 57 wt % free IL $[N_{6222}][Tf_2N]$ (relative to the total film mass), and 0.04 wt % DABCO (relative to the total film mass). These components were combined using the two-solution method described in the Experimental Section. Soak-in values were determined via mass analysis of the substrate, coating, and the container. No free IL $[N_{6222}][Tf_2N]$ was observed to leach from the cured films at room temperature.

3.4. Analysis of Curing by FT-IR Spectroscopy.
We investigated the curing time of the prepolymers **1a–d** and TDI under stoichiometric reaction conditions. To have practical use for first responders in the event of TIC spills, the coating must be able to cure in situ quickly (<60 min) to minimize exposure

to TIC vapors. The results of the FT-IR experiments are reported in Table 2.

Table 2. Curing Results of IL Prepolymer-Isocyanate Polymerizations As Determined by FT-IR Analysis[a]

ammonium-alcohol IL prepolymer used in curable coating mixture	curing time (min)
1a	33.7 ± 0.9
1b	18 ± 2
1c	11.3 ± 0.6
1d	7 ± 2

[a]Films contained prepolymers **1a–d** and TDI in the mass amounts needed to provide the same number of −OH and −NCO groups, 57 wt % free IL [N_{6222}][Tf_2N] (relative to the total film mass), and 0.04 wt % DABCO (relative to the total film mass). These components were combined using the two-solution method described in the Experimental Section. Curing times were determined as a function of the reduction of the area of the isocyanate IR stretching band at 2220−2330 cm^{-1} relative to an internal standard. The values shown are the averages of the results from 3 independent trials with standard deviation error bars.

On the basis of the results of the curing experiment, it was observed that the curing time decreased as a function of increasing prepolymer chain length. All of the observed IL prepolymer-based coatings were cured on a similar time scale to the previous small-molecule IL monomer system and required less DABCO catalyst to reach the observed gel point (0.01 molar equiv. or 0.04 wt % in the prepolymer system versus 0.1 molar equiv. or 0.89 wt % in the small-molecule monomer system).[17] The use of a curable IL prepolymer, furthermore, required less TDI cross-linking comonomer than the previous small-molecule system to reach the gel point. Because TDI is both toxic and readily reacts with water at ambient conditions, minimizing the amount of it used in the coating is advantageous for practical use.

3.5. Mechanical Testing. The mechanical properties of the prepolymer-based cured coatings were then investigated to determine their mechanical robustness and their ability to be applied to and removed from the substrates. The mechanical properties of the resulting bulk cured films were determined via dynamic mechanical analysis (DMA), and these results are summarized in Table 3. On the basis of the analysis of the stress−strain curves of the free-standing films, the E' values of the prepolymer-based free-standing cured films were on the same scale as the E' values of the films prepared using the small-molecule ammonium-alcohol IL monomers.[17] This result implies that there is similar flexibility between the two films. The σ_T values were much lower than the ammonium small molecule films. The small molecule films did not break until ∼1 MPa in a tensile test setup, while the most heavily cross-linked prepolymer film containing prepolymer **1c** broke at 0.46 MPa. This suggests that the cured films prepared using the IL-based prepolymers are significantly softer than the previously investigated films made from small-molecule monomers.

It was also observed that the initial (i.e., uncured) coating formulation prepared using prepolymer **1d** was a tacky solid that could not be applied to any substrate as a liquid. This is most likely due to its rapid curing time, and it cured too quickly to be effectively applied to the substrate. Despite its high retention of IL [N_{6222}][Tf_2N], formulations with prepolymer **1d** were removed from consideration as a possible

Table 3. Tensile Stress−Strain Results Measured for Prepolymer-Based, Free-Standing, Cured Films[a]

prepolymer used in film preparation	Young's modulus (MPa)	tensile strength (MPa)	elongation at break (%)
1a	1.5 ± 0.2	0.14 ± 0.01	15.1 ± 0.9
1b	3.4 ± 0.5	0.22 ± 0.02	10 ± 2
1c	9.1 ± 0.9	0.46 ± 0.06	14 ± 2

[a]Films contained prepolymers **1a–c** and TDI in the mass amounts needed to provide the same number of −OH and −NCO groups, 57 wt % free IL [N_{6222}][Tf_2N] (relative to the total film mass), and 0.04 wt % DABCO (relative to the total film mass). These components were combined using the two-solution method described in the Experimental Section. Stress−strain tensile tests were performed using standing films prepared using the two-solution method described above. The values shown are the averages of the results from three independent trials with standard deviation error bars. No free IL [N_{6222}][Tf_2N] was observed to leach from the cured films at room temperature.

curable coating system due to the practical limitations of substrate application.

3.6. TIC Simulant Hazard Mitigation Assays. Following the curing kinetics studies and mechanical characterization of the coatings, their effectiveness for organic TIC vapor suppression and liquid extraction from porous surfaces was tested. Previous research in our group on volatile organic chemical containment systems using IL-based coatings involved both physical gels[15] and covalently bonded polymer network gels.[16,17] The latter material was easy to remove from complex surfaces as a pliable solid film and showed promise in both TIC vapor suppression and uptake.[16,17] However, because the initially applied (i.e., uncured) coating utilized small-molecule ammonium monomers, the coating was unable to be applied to more porous substrates such as wood. Because of the porous nature of the substrate and the low viscosity of the initial coating prior to curing, the coating soaked through the substrate and did not form a solid film on top of the material. The use of larger molecular-weight reactive prepolymers (which would have some degree of chain entanglement in solution and thus higher viscosity at the same loading level) was explored to correct for this shortcoming of our initial coating materials.

We previously developed a series of GC−MS assays to test the TIC vapor containment and liquid uptake performance of curable IL monomer/TDI/IL-based coatings.[16,17] Vapor headspace studies involved the application of a known amount of a TIC simulant onto the substrate of interest, followed by the application of the initial reactive coating prepared using the two-solution method described above. The applied coating was allowed to cure for 24 h, followed by GC−MS analysis of the headspace above the coating to detect the presence of the TIC simulant. The liquid extraction studies involved removing the cured coating from the substrate, extracting the TIC simulant using an organic solvent, and sampling the solvent to determine the amount of TIC simulant remaining in the substrate. These two studies provide an idea of the TIC simulant vapor suppression and liquid uptake capabilities of our coatings. We subsequently used the same procedures to test the new ammonium-based curable prepolymer materials (see the Experimental Section and Supporting Information for details).

o-DCB was selected as the TIC simulant based on its structural similarity to polychlorinated biphenyls (PCBs),[32] which were once widely used as dielectric coolants in a variety of electronics.[34,35] They have since been identified as persistent pollutants and a danger to human health, and although their production and use have been globally banned, they remain an environmental threat due to their nonbiodegradability.[34,36−39]

The results of the *o*-DCB vapor containment studies for the new prepolymer-based, curable gel coatings are shown in Figure 1. Prepolymers **1a−c** were investigated in a set
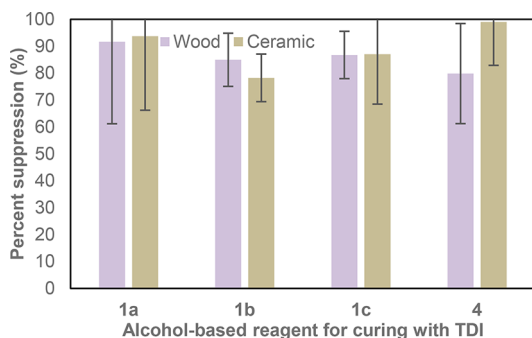
Figure 1. Results of the *o*-DCB vapor headspace assays of curable films prepared using prepolymers **1a−c** and TDI in the mass amounts needed to provide the same number of −OH and −NCO groups, 57 wt % free IL $[N_{6222}][Tf_2N]$ on wood and ceramic substrates contaminated with a set amount of *o*-DCB. An analogous curable coating formulated using small-molecule ammonium-triol IL monomer **4** instead of the IL prepolymer was investigated as a control material. The normalized fraction of gaseous *o*-DCB present in the headspace of the jar containing the coated substrates was compared to the fraction of *o*-DCB present in the headspace of the uncoated control. The values shown are the average values of three independent sample trials with standard deviation error bars.

formulations with TDI and IL $[N_{6222}][Tf_2N]$ (see Experimental Section for details), and the *o*-DCB vapor containment results of these applied coatings were compared to control coatings prepared with small-molecule ammonium-triol IL monomer **4** instead of an IL prepolymer. As noted in the prior section, a similar coating formulation prepared using prepolymer **1d** was not explored because it was a tacky solid that could not be applied to any substrate very well. All of the curable IL prepolymer-based films reduced the amount of *o*-DCB vapor released into the container headspace. Compared to uncoated control samples of the same substrate materials, upward of 80% of the *o*-DCB vapor was suppressed for the IL prepolymer/TDI/IL-coated wood and ceramic samples relative to the uncoated samples. These results are comparable to those achieved with the previously reported small-molecule imidazolium- and ammonium-alcohol IL monomer-based curable coating systems tested using the same TIC simulant vapor assay.[16,17] There was no discernible difference in vapor capping ability between coatings prepared from prepolymers of different molecular weights.

The liquid *o*-DCB extraction procedure used on the IL prepolymer/TDI/IL films was the same procedure used previously in our group.[16,17] The liquid *o*-DCB extraction results for the curable IL prepolymer/TDI/IL coating on wood and ceramic substrates are shown in Figure 2. In general, the IL prepolymer-based coatings applied to the wood substrates increased in extraction performance as the molecular-weight of the prepolymer decreased, with the wood sample treated with
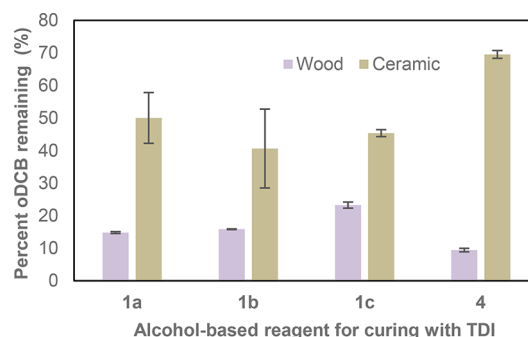
Figure 2. Results of the *o*-DCB vapor headspace assays of curable films prepared using prepolymers **1a−c** and TDI in the mass amounts needed to provide the same number of −OH and −NCO groups, 57 wt % free IL $[N_{6222}][Tf_2N]$ on wood and ceramic substrates contaminated with a set amount of *o*-DCB. An analogous curable coating formulated using small-molecule ammonium-triol IL monomer **4** instead of the IL prepolymer was investigated as a control material. The values shown are the average values of three independent sample trials with standard deviation error bars.

the prepolymer **1a**-based coating only containing 15% by mass of the originally applied *o*-DCB. The IL prepolymer-based curable coatings were all found to be less effective for removing liquid, soaked-in *o*-DCB from the ceramic substrates compared to the wood substrates, with significant amounts of *o*-DCB remaining in the former material. Coatings with prepolymers **1a−c** all had ∼40% of the originally applied *o*-DCB remaining in the ceramic substrate following the removal of the fully cured coating, with no discernible trend in effectiveness with variation in IL prepolymer molecular weight. The liquid extraction results for the ceramic substrate are on a similar scale to those observed in the rubber substrate investigated previously with the original ammonium-alcohol IL monomer/TDI/IL system.[17]

4. CONCLUSIONS

In summary, we have developed a new, curable, IL-prepolymer-based coating system for organic TIC vapor suppression and liquid TIC uptake that can effectively be applied to porous substrate surfaces such as wood and ceramic with minimal soak-in. This new curable coating system was found to cure quickly and effectively act as a suppressant for volatile organic TIC vapors as tested with *o*-DCB, a simulant for PCBs. Furthermore, the TIC extraction capabilities of this new coating system were similar to the small-molecule IL monomer/TDI/IL-based coatings previously developed by our group. Future work will include the investigation of using other IL materials, such as imidazolium ILs, in the IL prepolymer coating. Other goals include the minimization of hazards present in the coating such as the replacement of the Tf_2N^- anion and isocyanate monomer with less harmful chemical analogs.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b01292.

> Full NMR spectra and mass spectra for compound **3**; procedures for determining degree of polymerization and M_n values of ammonium IL-based prepolymers; information on test chamber setup used for *o*-DCB

vapor headspace and liquid extraction assays, example FT-IR spectra for film curing as function of time, example stress−strain curves of cured films; procedures used and example data obtained for the *o*-DCB vapor containment and liquid decontamination testing; example pictures of cured coatings removed from substrates; SEM images of porous wood and ceramic substrates used (PDF)

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Notes
The authors declare no competing financial interest.

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