Ammonium Binding Resins: Polymer-tethered Tetraphenylborate

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A novel approach to the problem of removing (organo)ammonium ions from industrial effluent and agricultural wastewater streams is proposed. Capitalizing on the insolubility of (organo)ammonium tetraphenylborate in water, we have designed, synthesized, and tested a polymer-tethered system that eliminates the ammonium ion from aqueous solution. Furthermore, the binding can be controllably reversed, thereby regenerating the material by deprotonating the ammonium ion in strong base, without significantly reducing the binding properties of the matrix. This work thus presents the synthesis and characterization of a polymeric system bearing anionic tetraphenylborate groups that reversibly sequester (organo)ammonium cations.

Introduction

The Nitrogen Cycle. Nitrogen and phosphorus are the two elements that control plant growth the most, restricting it when they are in low bioavailable supply.[1] The bioavailability of nitrogen is controlled by the nitrogen cycle and can be summarized as an equilibrium, facilitated by bacteria, between soil nitrates, ammonia, and atmospheric dinitrogen. Under normal conditions, soil nitrates and atmospheric dinitrogen together provide a sufficient source of ammonia for organic use. The growth of nitrifying bacteria is usually limited by the availability of ammonia, often strictly limited since these bacteria are in competition with other living organisms for the accessible supply. When the bacteria are given far more ammonia than is usual in the environment (for example in effluent water from some industries, or in water from sewage ponds) they prosper or *bloom*. This in turn leads to the deoxygenation of the affected ponds and the death of fish and other aquatic organisms.

Existing Technology for the Removal of Ammonia from Water. Since elevated ammonia levels can be highly toxic, there is clearly a need for an efficient “sponge” to mop-up after industrial chemistry and farming wastes. There are several such processes available. The centrate ammonium recovery process (ARP)[2,3] employs a proprietary ion-exchange system loaded with zinc that scavenges ammonia. Treating the system with sulfuric acid regenerates the ammonia. Not only does this make the ion-exchange system reusable, but also the resulting ammonium sulfate can be sold as fertilizer.

Examples of other patented materials and processes that have ammonium cleansing properties employ zeolites,[4] high-temperature and -pressure oxidation,[5] CO_2 extraction,[6] and microbial degradation.[7] The zeolite method requires many reaction chambers and addresses only NH_4^+ ions. High pressure and temperature reactions are expensive and require large on-site apparatus. Microbial degradation effectively reduces nitrogen-containing compounds to ammonia, but the efficient recovery of pure water is not trivial.[8]

Though a variety of procedures exist already for the purification of wastewater, there remains scope for an inexpensive, simple, re-usable alternative. The Dalhousie University X-ray Crystallography Center has had an ongoing interest in ammonium-containing structures for several decades, and in the course of their study of hydrogen bonding to phenyl π electrons, it was observed that the tetraphenylborate salt (TPB) of ammonium is highly insoluble in water. Low-temperature (120 K), X-ray diffraction studies[9] on NH_4TPB clearly indicate tetraradial boron centers with two pairs of orthogonal phenyl groups where the ammonium cation is trapped in a tetraphenyl cage between two boron hubs as shown in Figure 1. The NH_4TPB study has been extended to include many, more complex, nitrogen-containing species that can accept a proton and thus become cat-

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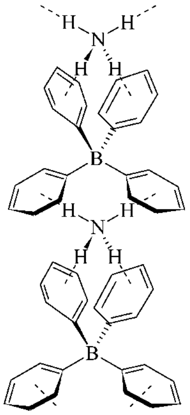

Figure 1. Schematic representation of ammonium tetraphenyl borate (ATPB) showing hydrogen bonding from the H(N)'s to the plane of the phenyl rings.

ionic.[10,11,12] The TPB anion is an effective scavenger not only for the ammonium ion but for (organo)ammonium and diammonium species as well as heterocyclic ammonium and even tetramethylammonium ions, and by extension, caffeine, nicotine, and other alkaloids including most street drugs.

When NaTPB(aq) is added in slight excess to a solution of ammonium chloride (200 ppm of NH_4^+), ammonium tetraphenylborate (NH_4TPB) precipitates and the supernatant is ammonium-ion free within the limits of colorimetric detection by Nessler's solution.[13−15] More quantitatively, mass spectrometric analysis was sensitive enough to detect ammonium in distilled water, yet showed no trace (<2 ppm) of ammonium in the NH_4-TPB supernatant.[16] The NaTPB/NH_4^+ reaction itself produces a precipitate that needs to settle, be completely filtered and then requires a separate treatment to recover the ammonia. To make the system practical and environmentally friendly, the TPB anion needs to be tethered to some substrate thereby removing the settling and filtering stage, thus simplifying the whole process.

Scope of this Paper. We describe here a method of tethering tetraphenylborate anions to a polymer matrix and show that these tethered anions reversibly sequester the ammonium ion. While small-molecule studies have demonstrated the wide range of organoammonium ions that will be trapped by the tetraphenylborate ion,[17,18] we have limited these initial polymer-tethered tetraphenylborate binding experiments to the simplest ammonium cation, NH_4^+.

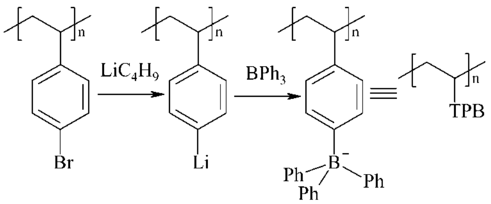

Figure 2. Reaction scheme indicating lithiation and triphenylboronation. The lithium counterion is ultimately replaced by sodium.

Using polystyrene as our basic starting material, we examined pathways by which this polymer support can be functionalized with TPB. To explore the synthetic chemistry, we started with commercially available non-cross-linked poly(4-bromo)styrene (P4BrS) and introduced BPh_3 at the 4-bromo position (Figure 2). This produced 300 mg of the initial polymer-tethered tetraphenylborate (PTPB-1).[19] Once it was established that a PTPB could be prepared, we then brominated cross-linked polystyrene (PS) beads and, as before, successfully attached BPh_3. These produced PTPB-2 in gram quantities, but with lower functionalization than the subsequent PTPB-3, where the quantity of material was 800 mg. All three PTPB samples were found to sequester the ammonium ion, and a series of successful sorption, desorption, and resorption experiments were completed with PTPB-2.

Experimental Section

The synthetic goal presented here was to produce cross-linked polymeric beads with tethered TPB groups. However, to test the feasibility of replacing a substantial fraction of the bromine atoms attached to the phenyl rings with BPh_3 groups as described below, we first examined reactions of non-cross-linked P4BrS that had been polymerized from monomeric 4-bromostyrene. With the issue of cross-linked polymer initially eliminated, the completely THF soluble P4BrS was an excellent substrate to test the triphenylboronation process.

From a number of possible routes for the synthesis of tethered TPB ions we chose to couple BPh_3, which is commercially available (Aldrich), and poly(4-bromo)styrene (P4BrS) by the reaction steps outlined in Figure 2. Ultimately a successful procedure for the tethering of BPh_3 to linear P4BrS via a lithiated intermediate was developed with the substitution of BPh_3 at a substantial fraction of the brominated aryl carbons (see below). The next step was to examine the same substitution reaction in the cross-linked polymer (PS). Brominated PS beads were not available and were therefore prepared from commercially available PS resin.

Bromination of PS Beads. We considered two routes to produce these brominated PS beads: (i) bromination of presynthesized cross-linked PS beads, or (ii) polymerization of styrene, (4-bromo)styrene, and divinylbenzene along with a pore-forming agent. We opted to brominate commercially available 200−400 mesh PS beads containing 2% divinylbenzene (DVB) (Polysciences) with iron(III) bromide.[20]

The beads were washed in hot THF (Soxhlet apparatus) for 24 h and were then dried in vacuo at 325 K. The PS beads (5 g) were suspended in CH_2Cl_2 with 500 mg of iron filings, and the reaction temperature was reduced to 273 K. Bromine (3 mL) was added in 1 mL aliquots, and after 1 h, the reaction temperature was raised to 313 K and left at reflux for 3 days.

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(19) Strictly speaking the pendant is sodium aryltriphenylborate; however, the name tetraphenylborate is retained to relate to the small molecule work.[9,10,17,18]

(20) *Caution!* The formation of iron bromide is exothermic, so appropriate precautions are required.

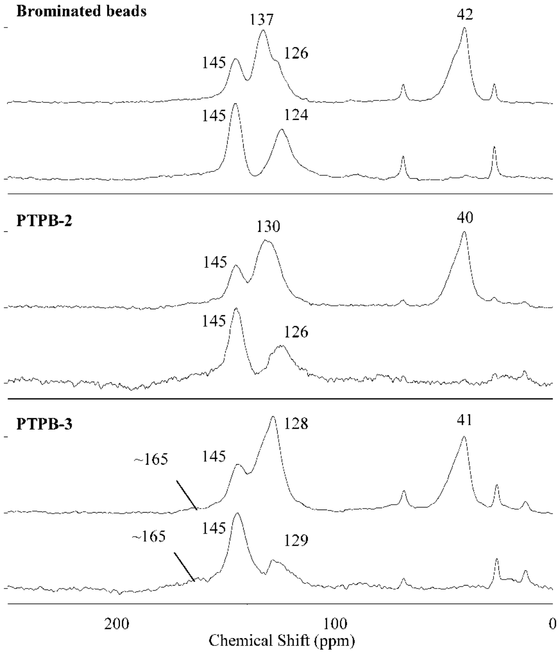

Figure 3. CP-MAS/TOSS (upper) and CP-MAS/TOSS/DD (lower) ^{13}C NMR spectra for three polymeric samples (top, brominated PS beads; middle, PTPB-2; bottom, PTPB-3). In the upper spectrum for each pair signals appear for all carbons, whereas the lower data indicate only the C_{Ar}−backbone and C_{Ar}−Br signals due to dipolar dephasing (gated decoupling).

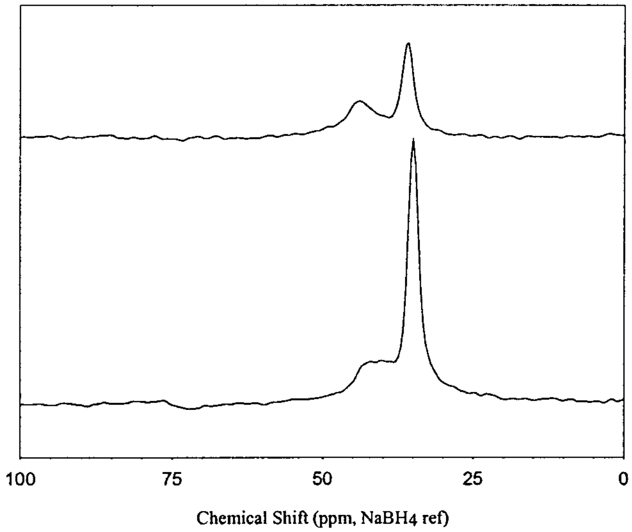

Figure 4. Solid-state ^{11}B NMR spectra of PTPB-2 (upper) and PTPB-3 (lower). The chemical shift is given relative to $NaBH_4$.

The product was washed in hot dichloromethane for 12 h and then extracted with hot THF for 3 days (Soxhlet). The sample was dried to constant weight, giving 9.6 g. Solid-state NMR spectra (see Figures 3 and 4) and FTIR data are described in the Characterization section below. The weight-fraction of bromine was determined by elemental analysis (QTI Technologies, Whitehouse, NJ) to be 52.7%, which corresponds well to the weight gain (48%). It seems reasonable, given the high bromine content, to conclude that surface bromination was accompanied by bromination within the beads. Ordinarily, alkyl-substituted phenyl rings are predisposed to ortho- or para-electrophilic aromatic substitution, though the para position is usually preferred for steric reasons. Once monobrominated, the carbons ortho to the bromine are the most susceptible to further bromination. It is therefore not surprising that the FTIR spectrum for the brominated beads, in the out-of-plane bending region, was consistent with the presence of both 1,4-disubstituted and also 1,2,4-trisubstituted aromatic rings, whereas the commercially polymerized P4BrS produced an FTIR spectrum with only 1,4-disubstituted phenyl bands. Since the bromination is a necessary precursor to the nucleophilic sites, maximum bromination was desirable.

The Aryllithium Intermediate. With the bromination successfully completed, it was necessary to develop a method for the introduction of BPh_3 at the 4-bromo site. Heterogeneous and homogeneous synthetic methods were considered for this reaction. Our initial attempts involved the formation of a nucleophilic Grignard with magnesium bromide at the para position of the PS phenyl groups, but this approach proved better adapted to small-molecule synthesis and the yield with the PS beads was poor. A better alternative to the synthesis of the polystyryl Grignard proved to involve the synthesis of the polystyryllithium intermediate as described by Braun et al.[21] The bromine−lithium exchange is a much more controllable reaction to run and for small molecules occurs at temperatures as low as 153 K. For small molecules, this chemistry is well established,[22] and it is often employed in the synthetic routes to monomer precursors. Pittman et al. have used similar chemistry in functionalizing polymer-supported catalysts.[23,24]

Lithiation and TPB Functionalization of Linear Homo-P4BrS. In a typical test reaction of linear homo-P4BrS, 240 mg (1.3 mmol of aryl bromide) of vacuum-oven dried polymer were dissolved in 20 mL of dry THF, freshly distilled from sodium/benzophenone, in an ultrapure nitrogen atmosphere. The reaction temperature was reduced to 265 K using a dry ice/acetone bath and 1.1 mL of a 1.3 M solution of *sec*-butyllithium (1.4 mmol) was added dropwise over several minutes.[25]

The reaction was left to stir at low temperature for several hours whereupon an aliquot was removed and quenched with acidified methanol/water. This initially gave a suspension of translucent organic droplets that gelled and solidified on stirring. Redissolution of the gel in THF was not possible, suggesting a cross-linked intermediate terpolymer of cross-linked styrene, debrominated styrene (via the lithiated product), and unreacted 4-bromostyrene. A new peak in the phenyl fingerprint FTIR spectrum at 700 cm^{-1} indicated the formation of the proton-trapped lithiation intermediate (styrene), and a diminished peak at 718 cm^{-1} suggested unreacted bromide.

Once the successful, albeit incomplete, lithiation of homo-P4BS had been established, conditions for the successful triphenylboronation of the linear polymer were as follows: 6.0 mL triphenylboron solution (0.25 M in THF or 1.5 mmol, Aldrich) was added to the lithiated polystyrene reaction mixture at 195 K and the reaction was allowed to warm to ambient conditions overnight. A sandy-colored precipitate with a faintly cloudy supernatant was observed 12 h after the triphenylboron addition.

The reaction was quenched in rapidly stirred distilled water giving rise to small solid particles (295 mg dry mass) (PTPB-1) for which IR spectra indicated successful functionalization (i.e., monosubstituted phenyl groups). The product was washed in NaCl(aq) to replace the lithium counterion for sodium. Both the polymeric starting material and regular homopolystyrene are very soluble in THF, yet the particles were only THF swellable and did not redissolve in any common solvent, suggesting that the product PTPB-1 was a cross-linked resin.

The aqueous fraction was blue-tinged (turbid) but otherwise transparent. On evaporation of the water, a film and some

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(25) Side reactions were anticipated due to the limited lithiating agent, but for ease of manipulation with the triphenylboron reaction that followed, we accepted the risk of cross-linking and spurious coupling.

solid residue remained suggesting triphenylboron side reactions and perhaps residual non-cross-linked polymer.

Lithiation and TPB Functionalization of PS-*co*-PDVB-*co*-PBrS. Several triphenylboronations of PS beads (PS-*co*-PDVB-*co*-PBrS) were carried out using the brominated PS beads prepared as described above. From the experience gained by reaction of the non-cross-linked P4BrS, the beads were functionalized as follows: PS-*co*-PVDB-*co*-PBrS (3.0 g containing 20 mmol of Ar−Br groups determined by elemental analysis) was stirred in 10 mL of dry THF, and the reaction temperature was reduced to 195 K. The lithiating reagent, *sec*-BuLi (17 mL, Aldrich, nominally 1.3 M) was added and the lithiation was allowed to proceed for 3.5 h whereupon 21 mmol of Ph_3B were added in THF and the reaction was allowed to warm to ambient conditions. Two days later, the reaction was quenched by addition of 4 M NaCl. The reaction mixture was filtered and then washed with THF, ethanol, and water and was finally dried to give 2.8 g of product (PTPB-2).

The highest degree of functionality was achieved under the following conditions: PS-*co*-PVDB-*co*-PBrS was dried in vacuo at 315 K overnight and 1.02 g (6.7 mmol Ar−Br) was suspended in 50 mL of dry THF. The reaction temperature was reduced to 195 K whereupon *sec*-BuLi (5.4 mL, 1.3 M in THF or 7.0 mmol, Aldrich) was added and the reaction was stirred for 75 min. Triphenylboron (BPh_3, 3.5 g) was dissolved in 50.0 mL of THF, as above, and the solution was added to the lithiated PS beads. The mixture was left to stir and warm to ambient temperature overnight until 20 h after initiation, when the reaction was terminated by addition of 2 mL Milli-Q water. The beads were stirred in 0.1 M NaCl for 24 h and were filtered. Soxhlet extraction (48 h, THF) was employed to wash the beads, which were then dried in vacuo at 325 K and weighed, yielding 0.78 g of PTPB-3.

Characterization

FT Infrared Spectroscopy. A Perkin-Elmer 16-PC FTIR using Spectrum software was used to collect FTIR spectra. With one exception, the samples were prepared as pellets with spectrograde KBr (Aldrich). The P4BrS precursor to PTPB-1 was cast as a film from THF on a KBr window (Wilmad). In all cases, the nominal resolution was 2 cm^{-1} and the number of scans was either 32 or 64.

To follow this series of reactions by FTIR is comparatively simple, since the degree of substitution[26,27] of a phenyl ring can be determined from the Ar−H out-of-plane bending region. Often, the fingerprint region (<1600 cm^{-1}), is too complicated for complete assignment. However, given the comparative simplicity of the starting material and the reaction scheme, most bands in these spectra can be identified with reasonable certainty. Where PS was the starting material, monosubstituted phenyl rings were expected, giving two characteristic bands at 770−730 cm^{-1} and 720−680 cm^{-1}. Para-disubstituted phenyl rings have a strong band at about 820 cm^{-1}.

FTIR spectra for the test reactions on the linear starting material (P4BrS) and its product, PTPB-1, indicated successful functionalization. After lithiation and triphenyl-boronation, the C−C sp^2 stretching region and the C−H in-plane distortion regions become more complex, reflecting the new phenyl groups, and the boron (mono)-substituted phenyl groups appear in the out-of-plane distortion region (especially 737 cm^{-1}). New peaks at 1430 and around 1240 cm^{-1} support the conclusion that the polymer has tetraphenylborate pendant groups.

Analysis of the FTIR spectra for PS beads (Polysciences) and brominated beads, PTPB-2 and PTPB-3, was uncomplicated. As one might expect, the PS beads gave a comparatively featureless IR spectrum with C═C stretches and both Ph−H in-plane and out-of-plane deformations that are characteristic of monosubstitution (i.e., pendant, but otherwise unsubstituted phenyl groups). A small peak at 840 cm^{-1} reflected the 2% 1,4-disubstituted divinylbenzene groups, and a band at 905 cm^{-1} may be due to unreacted vinyl groups. The spectrum of the brominated product showed evidence of 1,4- and 1,2,4-substitution, the monosubstitution bands being comparatively insignificant (e.g., at 755 cm^{-1}). After lithiation, the para position is preferentially occupied by triphenylborate. Other lithiated sites are sterically restricted by the extremely bulky boron moiety and therefore may be quenched during the workup with aqueous acid. As with PTPB-1, new peaks at 1436, ∼1240, and 737 cm^{-1} reflected the TPB groups. The TPB peaks were more pronounced relative to the neighboring peaks for PTPB-3 when compared with PTPB-2, suggesting a higher degree of functionalization.

Nuclear Magnetic Resonance Spectroscopy. Solid-state ^{13}C NMR spectra (CP-MAS[28] with TOSS[29] pulses) for the brominated PTPB-2 and PTPB-3 beads were obtained on a 300 MHz spectrometer (75 MHz for ^{13}C; see Figure 3) with a contact time of two or three milliseconds. The delay time between pulses was 2 s. Dipolar dephasing (DD, sometimes called gated decoupling) experiments were also employed to suppress nearly all signals from methylene and methane carbons atoms, leaving just quaternary, brominated phenyl, and methyl carbon signals.[30] Methyl carbon signals survive this experiment since C−H coupling for methyl groups is weak due to rotational relaxation. Boron-11 NMR spectra were collected for PTPB-2 and PTPB-3 (see Figure 4).

The successful bromination of the PS beads is supported by the residual peaks in the DD spectra (Figure 3) in the aromatic region where the carbon *ipso* to the backbone appears at 145 ppm and the brominated aromatic carbon appears at 124 ppm (C_{Ar}−Br ∼ 120 ppm).[31] Residual THF peaks (∼20 and 70 ppm) remain due to the mobility of the small molecules. The spectra in Figure 3 are normalized with respect to the backbone carbons near 40 ppm (upper spectrum in each pair). On this basis, the spectra for PTPB-2 suggest some additional phenyl groups when compared with the starting material (∼130 ppm in the CP-MAS/TOSS without DD). The PTPB-2 DD experiment indicates residual C_{Ar}-Br at 126 ppm. The carbon *ipso* to boron may appear as a very weak signal near 165 ppm (163.4 ppm for BPh_4^-, ^1J (^{11}B, ^{13}C) ∼ 50 Hz),[32] but positive assignment is not possible in these spectra due to the weakness of the resonance.

The aromatic carbons *ipso* to boron in PTPB-3 (Figure 3), on the other hand, do appear in both the CP-MAS/TOSS and CP-MAS/TOSS/DD spectra, though the DD spectrum still indicates residual brominated carbons (∼129 ppm). It should be noted that the intensities of the C−Br signals in the DD spectra for PTPB-2 and PTPB-3 are very much weaker than for the brominated beads.

The chemical shifts for the ^{11}B NMR spectra (see Figure 4) were assigned relative to $NaBH_4$, placing the boron signal for PTPB-2 and PTPB-3 around 40 ppm. ^{11}B has spin $^3/_2$, and the quadrupolar relaxation mechanism usually dominates. The Pake peak that one might expect for quadrupolar nuclei is reduced to a dominant sharp peak by the symmetry of the tetrahedral center. The second peak may be attributed to unsymmetrical arrangements caused by crowding and neighboring group effects. These boron NMR spectra thus confirm the presence of pendant TPB groups.

Samples of PTPB-2 and PTPB-3 with equal mass (80 mg each) were analyzed; thus, the peak heights are indicative of the relative degree of boronation. PTPB-2 appears to be less

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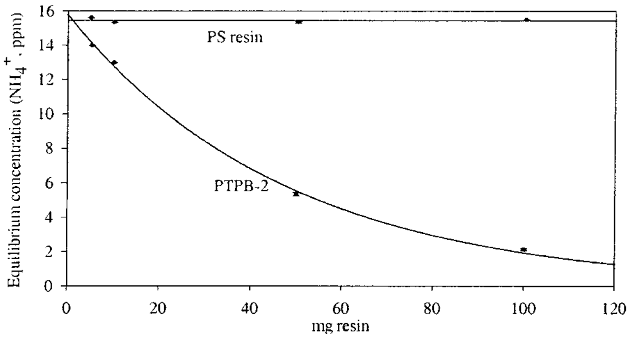

Figure 5. Ammonium sorption as a function of resin mass for PS and PTPB-2 in a 5 mL, 16 ppm (NH_4^+) solution.

functionalized than PTPB-3, a conclusion which is supported by the ammonium ion binding data that follow.

Binding

Nessler's Reagent and UV−Vis Colorimetric Assays. Nessler's reagent[33] is used to detect low concentrations of ammonia in water.[13−15] It is a strongly alkaline solution of mercury(II) potassium iodide (K_2HgI_4). The solution was clear and pale yellow in color. In the presence of ammonia, the color changed to dark orange as a function of the ammonium concentration and the change in absorbance at 412 nm was linear with concentration, all estimations of the ammonium ion concentration were determined at this wavelength. Deionized water (Milli-Q) was employed to prepare the solutions since it was critical that the water be as ammonia-free as possible.

All UV−vis data were obtained using an HP 8452A spectrometer interfaced to a PC and set to monitor absorbance at 412 nm. A quartz flow cell with a path length of 0.10 cm was used. Before each series of measurements, a Milli-Q water blank was run, and both the cell and the standards were calibrated by testing a 1.00 mL aliquot of each standard with 50 μL of Nessler's solution. Initially, each solution was injected four times and each injection was measured five times; however, the data showed that there was no significant variance between injections. Subsequent assays were injected once and were each measured several times. The data were plotted as absorbance vs [NH_4^+], and the linear regression provided a relation between absorbance and concentration. To accommodate absorbance values at extremely low ammonium concentrations (<5 ppm), a second-order fit was determined to follow the data most closely with the error on any given standard run being less than 2%. A first-order fit led to larger errors, particularly at low concentrations. Ammonium concentrations were determined in ppm for simplicity; however, the binding isotherms were reported in mmol; the conversion factor is 5.544×10^{-3} mM/ppm.

PS Beads: Control Experiment. To establish that the unfunctionalized starting material had no binding activity, four samples of PS beads (2% DVB, 200−400 mesh, Polysciences Inc.) weighing 5, 10, 50, and 100 mg each were shaken with 1.00 mL Milli-Q water for 24 h at which point 4.0 mL ammonium chloride solution (20 ppm) was added. The initial ammonium ion concentration was therefore 16 ppm. The suspension was agitated for 72 h and then the sample vials were centrifuged for approximately 15 min. Then 1.00 mL aliquots were withdrawn and tested with 50 μL of Nessler's solution. Absorbance data at 412 nm were converted to concentration values from the calibration data and were plotted as a function of resin mass. The data plotted in Figure 5 indicate that unfunctionalized PS beads have no sequestering effect on ammonium ion concentration.

Table 1. Summary of Polymer Samples and Ammonium Binding Values

sample[a]	maximum binding, Q_{max} (mmol/g)	binding constant, K (mM^{-1})	effective TPB-bearing groups, (%)
PTPB-1[i]	0.28	*n*/a	11
PTPB-2[ii]	0.18	1.64	7
PTPB-3[ii]	0.50	7.14	19

[a] Starting materials: [i]linear PS; [ii]200−400 mesh PS beads (Polysciences). Data for PTPB-1 are rough approximations.

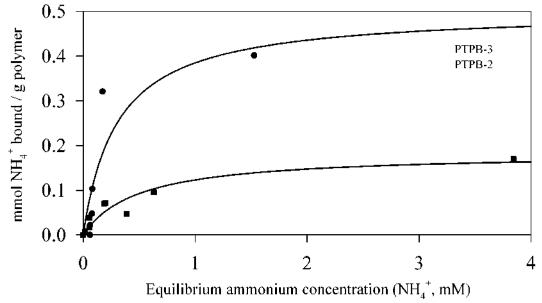

Figure 6. PTPB-2 and PTPB-3 ammonium sorption isotherms. Of note is the steep slope and the high plateau for PTPB-3, indicating strong binding and high capacity.

PTPB-1. To test the functionalized homopolymer for ammonium-binding properties, 2 mL of an aqueous solution of ammonium chloride (115 ppm) was added to 30 mg of the functionalized homopolymer and was stirred overnight in an airtight vial. Stock ammonium chloride solution (115 ppm) was diluted to 77 and 38 ppm. One drop of Nessler's solution was delivered to 0.30 mL of each standard as well as to 0.30 mL of distilled water. The colors observed ranged from orange (115 ppm) to colorless (0 ppm). The supernatant from the polymer assay was again tested in duplicate and the color generated was visually determined to be very slightly darker than that of the 38 ppm standard. The concentration of ammonium ions was therefore reduced by the polymer-bound tetraphenylborate to approximately one-third of its initial value. These preliminary and quasi-quantitative data correspond to a functional binding capacity of about 0.28 mmol of NH_4^+/g of polymer (see Table 1), or about 10% of the maximum possible capacity assuming triphenyl-boronation of every styryl monomer and that each pendant group binds one ammonium ion.

PTPB-2. Since several grams of PTBP-2 were synthesized, this sample was the subject of a series of ammonium sorption, desorption and resorption experiments. Initially, conditions identical to the control were employed for comparison. Four PTBP-2 samples weighing 5, 10, 50, and 100 mg each were shaken with 1.00 mL of Milli-Q water for 24 h at which point 4.0 mL of ammonium chloride solution (20 ppm) was added giving an initial ammonium ion concentration of 16 ppm. The suspension was agitated for 72 h. The sample vials were centrifuged for approximately 15 min, and 1.00 mL aliquots were withdrawn and tested with 50 μL of Nessler's solution. Absorbance data at 412 nm were converted to concentration values from the calibration curve and were plotted as a function of resin mass. A parallel experiment tested 10 mg samples of PTPB-2 with 2.0 mL aliquots of ammonium chloride solutions at 1, 5, 10, and 20 ppm (NH_4^+). To obtain more data points at lower equilibrium ammonium ion concentrations, larger PTPB-2 samples (50 mg) were also tested with 5 mL aliquots of ammonium chloride solutions at various initial concentrations. An ammonium ion binding isotherm was constructed from all PTPB-2 data (see Figure 6). The data were fitted with the Langmuir binding equation[34] of the form

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(33) Sometimes called Meyer's reagent. Note that in the presence of the tetraphenylborate ion, the ammonium ion specific electrode does not work reliably, and therefore, colorimetric analysis is required.

(34) Zhu, X. X.; Brizard, F.; Piché, J.; Yim, C. T.; Brown, G. R. *J. Colloid Interface Sci.* **2000**, *232*, 282−288.

$$[\mathrm{NH_4}^{+}{}_{\mathrm{bound(mmol/g)}}] = \frac{Q_{\max} K C_{\mathrm{eq}}}{1 + K C_{\mathrm{eq}}}$$

where $Q_{\max}$ gives the isotherm plateau (capacity), C_{eq} is the supernatant ammonium concentration (at equilibrium) and K is the binding constant (see Table 1).

Reusability. The sorption studies on PTPB-1 and -2 clearly indicate not only that the functionalization was successful, but also that the extraordinary insolubility of ammonium tetraphenylborate in water does indeed carry over to polymer systems. This alone makes the PTPB materials interesting given the ill effects of excess ammonium ions in the biosphere. However, a further necessary characteristic of an environmentally friendly polymer system is its reusability. In order for PTPB to be of any real industrial importance, it must be possible to strip any collected ammonium ions from the polymer and regenerate the system for subsequent reuse.

To determine if the ammonium ions could be stripped from the functionalized polymer without damaging the ability of the polymer to readsorb yet more ammonium ions, preliminary wet and dry desorption as well as resorption experiments with PTPB-2 and a weak base ($NaHCO_3$) were followed by quantitative desorption and resorption experiments with PTPB-2 and a strong base (NaOH).

Desorption: NaOH vs $NaHCO_3$. Two 100 mg samples of PTPB-2 were suspended in ammonium-containing solution (8 mL, 10 ppm). The final ammonium concentration in the supernatant was 1.8 ppm; therefore, each 100 mg sample bound 3.6 μmol of ammonium ion.[35] Each vial was centrifuged, and the supernatant was decanted. The residual resin in one vial was then suspended in 0.10 M $NaHCO_3$ (5.0 mL), while 0.10 M NaOH was added to the other sample (5.0 mL). After 75 min of agitation, 1 mL aliquots were filtered (0.45 μm filters) and assayed with Nessler's solution. As observed in preliminary assays with $KHCO_3$, the UV−vis absorbance from the $NaHCO_3$ exposed aliquots increased dramatically with successive scans. The values for ammonium concentration increased from 3.2 ppm to more than 10 ppm over the course of 10 scans despite a delay of 5−10 min between the addition of Nessler's solution and collection of the UV data. The sample in the cell was visibly turbid and sonication was required to render the cell clean. Clearly, the resultant colorimetric assays for bicarbonate-mediated regeneration are unreliable.

Although the bicarbonate assay with Nessler's solution was not photostable leading to a cloudy solution and ultimately, precipitation, the hydroxide-containing assay was unsurprisingly robust (Nessler's solution is ~4 M in NaOH). The final ammonium concentration that resulted for the first washing was 4.5 ppm and the final ammonium concentration for the second washing was 3.94 ppm. Since the concentration reduction for the pre-loading in 8 mL was from 10 to 1.8 ppm, the total sorption was 8.2 mg/L in a volume of 8 mL, or 66 μg. The desorption for the first washing was 23 μg and for the second, 20 μg: i.e., 43 μg representing about 67% of the total. Therefore, a maximum activity of 70% (compared with previously unexposed material) was anticipated for the reactivated PTPB-2.

Resorption: Hydroxide-Washed Beads. A resorption experiment with the hydroxide-washed beads was employed to determine whether the base wash was destructive to the polymer. The resin recovered after being treated with hydroxide was washed with Milli-Q water, filtered, and divided among three vials (9 mg, 25 mg and 37 mg). A solution containing ammonium ions (5.0 mL, $[\mathrm{NH_4}^+] = 10$ ppm) was added to each vial, and the sample was agitated for 6 h. The supernatant ammonium concentration and binding values were determined as before (see Table 2).

The ammonium binding values for PTPB-2 after the hydroxide wash are given in Table 2. Once corrected to reflect the incomplete liberation of ammonium ions during the hydroxide wash (~70%), these data show that despite having been exposed to 0.1 M NaOH, PTPB-2 retains a significant fraction of its initial activity. Furthermore, the incomplete activity regeneration of PTPB-2 may also have been a reflection of the protracted exposure to strongly basic hydroxide anions (~80 h), which may have been partially destructive with respect to the binding sites. While these experiments demonstrate the uncomplicated reusability of the PTPB resins, the parameters were by no means optimized due to limited material. The PTPB samples thus show promise as ammonium scavengers.

Table 2. Bound Ammonium Ion as a Function of Regenerated PTPB-2 Resin Mass and Activity Comparing Initial Sorption Data with Resorption Data Following a Hydroxide PTPB Regeneration

PTPB-2 mass (mg)	$\mathrm{NH_4}^+$ C_{eq} (mM)	$\mathrm{NH_4}^+{}_{\mathrm{(bound)}}$ PTPB−2 (mmol/g)	activity (%)[a]	$\text{activity}_{\text{norm}}$ (%)[b]
8.6	0.46	0.052	58	82
25	0.38	0.034	42	60
37	0.20	0.023	32	46

[a] When compared with the activity of "virgin" PTPB-2. [b] The activity normalized to reflect the incomplete ammonium ion liberation (70%).

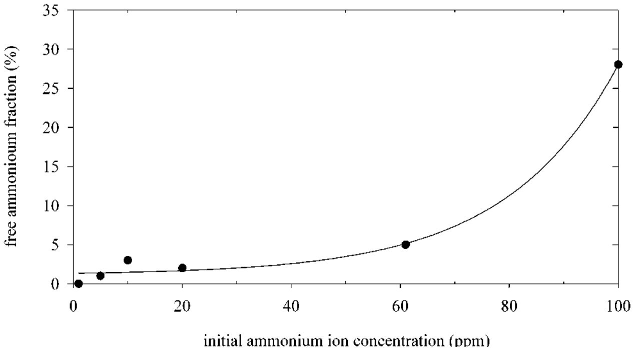

Figure 7. Unbound ammonium fraction vs $[\mathrm{NH_4}^+]^{\mathrm{i}}$ for PTPB-3. Under these experimental conditions (50 mg PTPB-3, 5 mL NH_4Cl solutions at $C_{\mathrm{i}} = 1-100$ ppm) even where sorption is not quantitative, the free ammonium fraction remains very low.

PTPB-3. As indicated by the FTIR and NMR spectra, PTPB-3 was more heavily functionalized than PTPB-2. To mimic the study for PTPB-2, 50 mg samples of PTPB-3 were prepared, to which 5.0 mL of solutions containing ammonium ions were added at the following concentrations (in ppm): 1, 5, 10, 20, 61, and 100. In the first instance, only 1−20 ppm solutions were employed; however, since the sorption was essentially quantitative after only 3 h, additional samples with 61 and 100 ppm solutions were prepared and tested following 48 h of agitation (see Figures 6 and 7).

The isotherm shown in Figure 6 shows that PTPB-3 effectively binds ammonium ions. The steep slope at low concentrations is indicative of strong binding (see Table 1), consistent with the data shown in Figure 7. The plateau at approximately 0.5 mmol/g of dry polymer suggests that at slightly elevated equilibrium concentrations, virtually all of the available sites are binding ammonium ions. Although an absolute value for functionality is not available, estimates based on molar masses indicate that the maximum that can be expected is 2.6 mmol/g ignoring the presence of cross-linking.

Quantitative binding appears to take place up to an initial ammonium concentration of about 60 ppm; however, binding is significant, even up to 100 ppm (see Figure 7). After the addition of PTPB-3 to an NH_4Cl solution ($[\mathrm{NH_4}^+]_{\mathrm{i}} = 100$ ppm) the final supernatant concentration was about 30 ppm (70% of the initial ammonium ions were removed from solution). Without dilution, measuring 60 ppm ammonium ion concentrations is near the upper limit of the Nessler reagent under these conditions. At higher concentrations, a solid orange precipitate was observed.

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(35) The conversion factor is 5.54×10^{-5} mol L^{-1} $\mathrm{ppm}^{-1.}$

Sorption Discussion

The utility of PTPB materials for the extraction of ammonium ions from aqueous solution depends on several factors including (i) strong binding that can be "switched off" , to regenerate the material, and (ii) high capacity. The strength of the binding is a function of the matrix and most importantly the interaction between the binding moiety and the sorbate. The solubility of NH_4TPB (the untethered form) in water is so low as to be essentially immeasurable; therefore, it is comforting that the binding isotherms for the PTPB systems (the tethered forms) indicate equally strong binding. Clearly, PTPB is an excellent ammonium ion scavenger since once the tethered phenyl cage has entrapped an ammonium ion (see Figure 1), the ion is essentially completely removed from solution. Thus, the ammonium ion sequestering effect of the free tetraphenylborate anion continues even when the anion is tethered to the polymeric backbone.

The capacity of the material to absorb the ammonium ion appears to be determined by the degree of functionality. Notwithstanding the restricted use of lithiating agent, indications are that the fraction of PTPB-1 repeat units bearing TPB is substantial due to at least two factors. Not only was the original starting material uniformly and completely monobrominated, but also the earliest visual indication of cross-linking during the functionalization process came after the addition of triphenylboron. Therefore, all potential sites were in intimate and free contact with the reagents. The scale of this trial (300 mg) rendered more extensive binding assays impossible, but the results gave clear evidence for the formation of tetraphenylborate functional groups and were sufficiently encouraging to warrant the functionalization of PS beads.

The data from the PTPB-2 sorption trials (see Figure 6) indicate the potential effectiveness of the binding sites (cf. FTIR discussion above). The minimum bound fraction of ammonium ions from 5.0 mL of NH_4Cl solutions was 30% following addition of 50 mg PTPB-2. At very low ammonium concentrations, the sorption efficiency is much higher ($\sim$75% at $[NH_4]^i = 4$ ppm). For PTPB-2, the ammonium-binding constant appears to be much lower than for free TPB anions, which may be explained by considering the PTPB-2 degree of functionality and the NH_4TPB crystal structure. For the small molecules, NH_4^+ and TPB^- can form highly regular H-bonded columns where each ammonium ion is held in a cage of four electron-rich phenyl groups. Since the FTIR spectra suggest that the functionality of PTPB-2 is lower than for PTPB-3, it is possible that π-H bonding is insufficient to produce the quantitative ammonium extraction observed for free TPB anions due to the restricted availability and mobility of cage-forming phenyl groups. The binding isotherm plateau is at about 0.18 mmol per gram PTPB-2. If PTPB-2 were completely functionalized, it would provide 2.7 mmol binding sites per gram, ignoring the presence of cross-linking. Thus, a conservative estimate[36] of the functionality of this polymer is 7%. The scale of the PTPB-2 functionalization permitted a series of experiments confirming the re-usability of the material as described above.

The PTPB-3 functionalization reaction was designed to increase the degree of triphenylboron incorporation into the polymer matrix and this material outperformed both PTPB-1 and PTPB-2. Even beyond the quantitative binding regime, significant ammonium reduction was observed (0.4 mmol of ammonium/g of PTPB-3). The fraction of TPB-bearing repeat units for this polymer was at least 19%. Although not conclusive, quantitative binding for a more heavily functionalized polymer supports the hypothesis that increased availability of phenyl groups makes phenyl cages for the ammonium ions possible. It is also probable that the elevated degree of functionalization favors binding within the polymer matrix. Any cross-linking as a result of the nonideal lithiating conditions will have had a deleterious effect on the binding capacity of the material since potential sites are consumed, the segmental mobility is decreased and the diffusion of ammonium ions into the beads will be restricted. The optimization of functionalization and regeneration are the subject of ongoing study, and we expect that the regeneration of PTPB-3 would parallel that of PTPB-2.

Summary

(Organo)ammonium species can be an environmental threat and range from the simple, yet potentially devastating NH_4^+ ion, to more complex molecules including the alkaloids. Present technologies available to scavenge ammonium ions from water tend to suffer from high cost and are not applicable to many situations. A need remains for an inexpensive, environmentally friendly, reusable system to clean wastewater; polymer-tethered tetraphenylborate represents a viable option.

We have presented a method for the successful synthesis of polymer-supported TPB and have demonstrated its effectiveness. Earlier studies have shown that TPB sequesters virtually all (organo)ammonium ions even without the rigorous "cage" presented schematically in Figure 1.[10,16−18] We expect that the wide range of species trapped by TPB in the small-molecule system will translate to a similarly wide range of species trapped by the tethered-TPB. We began by exploring the synthetic method and binding characteristics of the system on a linear homopolymer (PTPB-1) and then worked exclusively with 200−400 mesh PS beads (PTPB-2 and -3). Unfunctionalized PS beads were shown to have no ammonium-binding capability. When the functionalization was comparatively low (PTPB-2), the ammonium-scavenging characteristics were not optimal and the binding appeared to be somewhat reversible in aqueous environments. The ^{11}B NMR spectrum of this sample suggests that there are two environments for boron, and therefore, the low activity may well be due to the limited availability of TPB pendants. At very low concentrations, the sorption is on the order of 75%; but at slightly elevated initial ammonium ion concentrations, only 30% of the ammonium was sequestered. The binding isotherm plateau occurred at about 0.18 mmol of NH_4^+/g of PTPB-2. Desorption and resorption experiments on PTPB-2

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(36) This assumes that one binding site binds one ammonium ion and that all binding sites are occupied.

confirm that the ammonium can be stripped from the polymer and that the most of the previous activity is regained.

Spectroscopic analysis including ^{13}C and ^{11}B NMR, as well as FTIR spectroscopy, forecast the dramatically increased activity of PTPB-3. For this polymer, ammonium sorption appears to be quantitative within the limits of the functionality ($\sim$0.4 mmol of NH_4^+/g of resin).

Note in Memoriam. G. Ronald Brown died unexpectedly just as this manuscript was being completed. His input to the work was invaluable and he will be sorely missed as a supervisor, friend, and collaborator. A generation of students and colleagues at all levels benefited from his insightful interactions; the personal and scientific loss is immeasurable.

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