Boric Acid Recovery Using Polymer Filtration: Studies with Alkyl Monool, Diol, and Triol Containing Polyethylenimines

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ABSTRACT: Three water-soluble polymers containing linear alkyl monool, 1,2-diol, and 1,2,3-triol groups, mostly on the primary amines of polyethylenimine, were synthesized, characterized, and tested for their ability to recover boric acid. The boron-binding capacities of these polymers and the backbone polyethylenimine were determined by titration, ultrafiltration, and inductively coupled plasma/ atomic emission spectroscopy analysis. At low boron concentrations, the 1,2,3-triol polymer performed better than the 1,2-diol, whereas at high boron concentrations, the 1,2-diol outperformed the 1,2,3-triol. ^{11}B-NMR spectroscopy and retention studies with various salt concentrations indicated that boron interacted with these two polymers by means of ion pairing with the protonated amines and by borate ester formation. For the monool and the polyethylenimine backbone, the mechanism for boron binding was ion pairing only. These polymers are under consideration for the selective recovery and recycling of enriched boric acid used in the primary coolant loop of pressurized water nuclear reactors. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1590–1604, 2005

Key words: membranes; separation techniques; water-soluble polymers

INTRODUCTION

Boric acid (BA) serves as an adjustable neutron-absorbing additive in the primary coolant water of pressurized water reactors (PWRs).[1] The movement of the nuclear power industry to longer fuel cycles and higher fuel burn-up requires higher coolant water BA concentrations. Higher lithium-7 hydroxide (^{7}LiOH) concentrations are necessary to maintain the pH in a range to minimize corrosion and yet are associated with increased stress corrosion cracking in the primary coolant loop and Zircaloy fuel-cladding corrosion.[2,3]

The use of ^{10}B-enriched boric acid (EBA) has been proposed for a number of years as a way of reducing the required concentrations of BA and associated ^{7}LiOH.[4] The lighter isotope of boron, ^{10}B (20% natural abundance, 3837 barns cross section), has a neutron absorption cross section many times greater than that of ^{11}B (80% natural abundance, 0.005 barns cross sec-

tion). The high cost of EBA necessitates a means of cost-effectively recovering and reusing it.[5] Presently, natural BA is removed from the primary reactor coolant system with anion-exchange resins as fuel burn-up increases. BA and other anionic contaminants are discarded along with the anion exchanger when the resin capacity is reached. Boron-selective absorbents for the recovery of EBA are of interest to the nuclear power industry.

Polymer filtration (PF) is a low-pressure, membrane-based separation technology that employs ultrafiltration (UF) in concert with high-molecular-weight, water-soluble, solute-binding polymers. This technology, known by a variety of names, has the potential to become a viable process for selective EBA recovery and recycling through the development of appropriate water-soluble, boron-binding polymers.[6–11]

Water-soluble polymers are generally used in the PF process on a low weight-to-volume basis (ca. 1%) to maintain reasonable membrane flux rates.[8] An important polymer-design feature is to obtain high boron-binding constants, selectivity, and capacity at the lowest average-repeat-unit molecular weight (ARU MW). However, binding constants must not be so large that BA will irreversibly bind to the polymer; this is a particularly complicated issue for nuclear power ap-

plications as ultrapure waters are required in the primary coolant loop.[1] Polymers that are selective to boron binding have most often been prepared by the attachment of sugar-like polyol ligands to polymeric backbones for both resins and soluble polymers.[9,12–15] In general, the stability of borate esters is enhanced as the number of vicinal hydroxy groups increases.[16] Concurrently, as the number of hydroxy groups increases, so does the ARU MW. Consequently, a compromise between a large number of linear hydroxy groups and a low ARU MW should be achieved. Thus, when hydroxy-functionalized polymers are designed for selective boron binding from linear alkyl polyols, it is useful to have the minimum number of vicinal hydroxy groups necessary to form sufficiently stable boron adducts.[17,18]

Derivatives formed from the direct monofunctionalization of primary (1°) amines on polyethylenimine (PEI) with simple, linear alkyl hydroxy- and polyhydroxy-containing ligands were synthesized as water-soluble polymers for binding BA in our studies. Hydroxy-functional-group attachment through an oxirane ring-opening reaction is advantageous, in that it forms stable C—N bonds, in comparison with functional-group attachment through potentially hydrolyzable ester or amide bonds.[9] A simple one-step functionalization reaction occurs in water, allowing the product to be directly purified by UF. PEI is a hyperbranched polymer that is nearly spherical and more amenable to UF because its solution viscosity is lower than that of linear polymers.[9,19] The average repeat unit (ARU) in PEI has a low molecular weight (MW), and this helps to maintain a high functional capacity. In this article, we report the synthesis, characterization, BA binding properties, and comparison of monool-, 1,2-diol-, and 1,2,3-triol-PEI polymers developed to reversibly bind boron for use with the PF process.

EXPERIMENTAL

Chemicals

Propylene oxide, 3,4-dihydroxybutene, *m*-chloroperbenzoic acid (57–89% with water), potassium carbonate (99%; Aldrich, Milwaukee, WI), ethanol (anhydrous), acetone, magnesium sulfate (Baker, Phillipsburg, NJ), *p*-toluene sulfonic acid (96%; Eastman, Rochester, NY), chloroform (Burdick & Jackson, Muskegon, MI), petroleum ether (bp = 30–60°C), sodium sulfate, sodium bisulfite, sodium bicarbonate, sodium chloride (Fisher, Fair Lawn, NJ), *n*-butylamine, diethylamine (>99%; Janssen Chimica, Fair Lawn, NJ), and triethylamine (99%; Aldrich) were used as received. Glycidol (96%; Aldrich) was freshly vacuum-distilled before use. NMR solvents and standards, chloroform-*d* (99.9 atom % D), D_2O (99.9 atom % D), 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt, and 3-(trimethylsilyl)-propionic acid-D4, sodium salt (TSP) (98 atom % D; Aldrich) were used as received. Deionized (DI; >17 MO) water was used for all solutions. Calibration standards for inductively coupled plasma/atomic emission spectroscopy (ICP–AES) were prepared by the dilution of aliquots of a 1000 ug/mL borate standard (SPEX, Metuchen, NJ). pH values were adjusted with hydrochloric acid (Fisher) and sodium hydroxide (VWR, West Chester, PA). All polymer concentrations are given as weight-to-volume percentages.

Equipment

The instruments and equipment included an analytical balance (model AC 100, Mettler, Columbus, OH), a UF unit [quick-stand bench top with a 30,000 molecular weight cutoff (MWCO) membrane; AG Technologies, New York, NY], a freeze dryer (model Freezone 4.5, Labconoco, Kansas City, MO), Fourier transform infrared equipment (FTIR; Avatar 360, Nicolet, Waltham, MA and Galaxy Series 5000, Mattson, Waltham, MA), an evaporator (RE 120, Buchi, New Castle, DE), autopipettes (10.00-mL, 2.500-mL, 250.00-μL, and 25.00-μL electronic digital pipettes; Rainin, Columbus, OH), a pH meter (model 210A, model 520A, and Ross L Combination model 81-C2 pH electrode, Orion, Waltham, MA), a stirrer and hotplate (Corning, Corning, NY), a centrifuge (model 5810R, Eppendorf, Westburg, NY), UF cartridges (MWCO = 10,000; Centricon-10 microconcentrators, Amicon, Bedford, MA), ICP–AES equipment (IRIS, Thermo Jarrell Ash, Waltham, MA), and DI water purifiers (minimum resistivity = 17.5 MO cm at 25°C; Barnstead e-pure, Culligan, Northbrook, IL).

Preparation of PEI

PEI (ca. 5% solution; water-free Polymin, BASF, Florham Park, NJ) was purified by diafiltration with 5 vol equiv of DI water through a 30,000 MWCO membrane and was concentrated.[20] The percentage of the polymer in the retentate, determined by the drying of an aliquot of the solution, was about 10%. This polymer was used as the backbone polymer for the hydroxy-functionalized polymers. PEI was calculated as a four-nitrogen-containing ARU with an MW of 172 g/mol based on the manufacturer's specification that the material consisted of a 1:2:1 molar ratio of 1°, 2°, and 3° amines.

^{1}H-NMR (400.13 MHz, D_2O, TSP): 2.60–2.76 ppm (br).

Preparation of the monool-PEI polymer

Chilled propylene oxide (2.9 mL, 0.043 mol; bp = 35°C) was added to a chilled 10.7% aqueous PEI

solution (0.17 mol) in a round-bottom flask over a 5-min period while the mixture was stirred under nitrogen. After the ice bath was removed, the mixture was stirred at room temperature overnight and then heated at 50°C for 3 h. The resulting colorless product was placed *in vacuo* at 50°C to remove volatile starting material. The reaction product was purified by diafiltration with 5 vol equiv of DI water through a 30,000 MWCO membrane. The final weight was 82.8 g of solution or approximately 12.6% monool-PEI polymer solution, which was used for further studies. The four-nitrogen-containing ARU MW was 230 g/mol, and the PEI was considered 25% functionalized.

^{1}H-NMR (400.13 MHz, D_2O): 1.20–1.28 (m, 5H, CH_3), 2.56–2.8 (br, 30H, CH_2), 3.98 (br, 2H, **CH**OH).

Preparation of the 1,2-diol-PEI polymer

Glycidol (31.5 g, 0.425 mol) was added to a 10.7% aqueous PEI solution (683.75 mL, 1.699 mol) in a 1-L, round-bottom flask over a 10-min period at room temperature. The solution was stirred for 2 h with heating to 100°C and then was cooled to room temperature overnight. The solution was diafiltered through a 30,000 MWCO membrane with 5–6 vol equiv of water. The product volume was reduced to 473 mL, and this yielded a 12.7% solution of the 1,2-diol-PEI polymer, which was used in further testing. The ARU MW was 246 g/mol, and the PEI was about 25% functionalized.

^{1}H-NMR (400.13 MHz, D_2O): 2.5–2.7 (18H, CH_2), 3.39, 3.40, 3.45, 3.48 (2H, m, **CH$_2$**OH), 3.68 [1H, **CH**(OH)].

Preparation of the 1,2,3-triol-PEI polymer

Ketal formation

3,4-Dihydroxybutene (8.8 g, 0.1 mol) was placed in a 250-mL, round-bottom flask equipped with a magnetic stirrer, a heated oil bath, and a Dean–Stark apparatus topped with a $CaCl_2$ drying tube. Acetone (7.3 mL, 0.1 mol), *p*-toluene sulfonic acid (5 mg), and petroleum ether (100 mL) were added, and the mixture was stirred under reflux overnight while the water/petroleum ether azeotrope was removed. The resulting solution was decanted from a small amount of brown residue, dried over K_2CO_3, and filtered. The solvent was removed by column distillation to give 11.0 g (90% yield) of 3,4-dihydroxybutene-acetoketal with no diol starting material remaining according to the IR spectrum (loss of 3351.9 cm^{-1}).

bp: 44°C at 28 mm. FTIR cm^{-1} (neat): 1062.6 (s), 2987.3 (s), 1216.7 (s), 1371.2 (s), 859.3 (s), 1380.3 (s), 1156.8 (s), 928.1 (m), 989.1 (m), 2873.1 (m), 2936.6 (m), 3084.2 (w, HC=C), 1647.0 (w, C=C). ^{1}H-NMR (199.884 MHz, CDCl$_3$, tetra methyl silane (TMS)): 1.39 (3H, m, Me), 1.43 (3H, m, Me), 3.56–4.14 (2H, m, CH$_2$),

4.45–4.55 (1H, m, CH), 5.19–5.40 (2H, m, CH$_2$-vinyl), 5.75–5.92 (1H, m, CH-vinyl). ^{13}C-NMR (^{1}H-coupled and {^{1}H}, 50.266 MHz, CDCl$_3$, TMS): 25.77 (qq, Me, J_{CH} = 126.67 Hz), 26.55 (qq, Me, J_{CH} = 126.62 Hz), 69.18 (t, CH$_2$, J_{CH} = 147.63 Hz), 77.29 (d, CH), 109.24 (s, C), 117.89 (t, CH$_2$-vinyl, J_{CH} = 156.03 Hz), 135.8 (dm, CH-vinyl, J_{CH} = 151.80 Hz).

Epoxidation

The previously prepared 3,4-dihydroxybutene-acetoketal was placed in a 1-L, round-bottom flask equipped with a magnetic stirrer, an ice bath, and a condenser. *m*-Chloroperbenzoic acid (77%, 22.5 g, 86 mmol) was dissolved in chloroform (217 mL), the water phase was separated and removed, and the solution was dried through a plug of anhydrous sodium sulfate. The dried peracid in a chloroform solution (0.05*M*) was added to the cold, vigorously stirred reaction solution over 2 h with an addition funnel. The mixture was heated to reflux on a steam bath (65°C), and 30 mL of chloroform and water were collected in a Dean–Stark apparatus. The solution was refluxed for 3 h, and the reaction was cooled over night at room temperature. The reaction was further cooled in ice to complete the precipitation of the *m*-chlorobenzoic acid, which was collected by filtration. The chloroform solution was washed three times with 30 mL of 20% sodium bisulfite, three times with 30 mL of 10% sodium bicarbonate, and once with 25 mL of saturated sodium chloride. The solution was dried over magnesium sulfate and filtered. The solvent was removed at room temperature on a rotary evaporator. The epoxide product (15.5 g) appeared by IR to contain a little solvent. Half of the product was distilled, and this produced 5.7 g (93% yield).

bp: 88°C at 30 mm. FTIR cm^{-1} (neat): 1063.7 (s), 851.0 (s), 1214.6 (s), 1371.9 (s), 1256.0 (s), 2988.0 (s), 1155.7 (s), 898.8 (s)2935.7 (m), 24,5 (m), 3057.4 (w, CH-epoxide). ^{1}H-NMR (400.13 MHz, CDCl$_3$, TMS): 1.34 (3H, t, Me, *J* = 0.8 Hz), 1.42, 1.43 (3H, t, t, Me, $J_{(s)}$ = 0.5 Hz), 2.61–2.65 (1H, m, CH$_2$-epoxy), 2.74–2.83 (1H, m, CH$_2$-epoxy), 2.99–3.02 (1H, m, CH-epoxy), 3.81–3.97 (2H, m, CH$_2$), 4.06–4.13 (1H, m, CH). ^{13}C-NMR (^{1}H-coupled, 50.27 MHz, {^{1}H}, 100.61 MHz, CDCl$_3$, TMS): 24.79 (q, Me, J_{CH} = 126.6 Hz), 25.03 (q, Me, J_{CH} = 126.6 Hz), 25.93 (q, Me, J_{CH} = 126.9 Hz), 26.03 (q, Me, J_{CH} = 126.9 Hz), 43.11 (t, CH$_2$-epoxy, J_{CH} = 176.7 Hz), 44.96 (t, CH$_2$-epoxy, J_{CH} = 175.7 Hz), 51.44 (d, CH-epoxy, J_{CH} = 175.4 Hz), 51.46 (d, CH-epoxy, J_{CH} = 175.4 Hz), 65.47 (t, CH$_2$, J_{CH} = 147.0 Hz), 66.25 (t, CH$_2$, J_{CH} = 150.3 Hz), 75.79 (d, CH, J_{CH} = 151.9 Hz), 75.90 (d, CH, J_{CH} = 151.9 Hz), 109.15 (s, C), 109.40 (s, C).

PEI addition

The previously prepared epoxide (2.2 g, 14 mmol) was added to a 10.3% aqueous PEI solution (23.7 mL, 56 mmol) in a round-bottom flask over a 10-min period with stirring under nitrogen. Ethanol (12 mL) was added to complete the dissolution of the reagents, and the solution was stirred at room temperature for 9 h; this was followed by heating on a rotary evaporator at 40°C for 2 h to remove the ethanol. Water (12 mL) was added to the clear, colorless solution, which turned light yellow when it was made acidic (pH 3–4) with 6N HCl. Complete ketal hydrolysis was verified by NMR spectroscopy (loss of methyl groups) after 6 h of stirring at room temperature and 1 h of heating to 60°C. To ensure the removal of HCl from the amines on the polymeric backbone, base was added (1M NaOH), and the solution was diafiltered through a 30,000 MWCO membrane with 5–6 vol equiv of 1M NaOH; this was followed by diafiltration with DI water until the permeate was neutral. The product was freeze-dried, 3.5 g (90% yield) of a yellow solid was yielded. The ARU MW for the 1,2,3-triol-PEI compound was considered to be 276 g/mol, and PEI was about 25% functionalized.

^{1}H-NMR (400.13 MHz, D$_2$O): 2.69, 2.75 (18H, CH$_2$), 3.62, 3.63, 3.64, 3.76, 3.77, 3.79 [4H, m, C**H**(OH)C**H**(OH)C**H$_2$**(OH)].

NMR measurements

^{1}H- and ^{13}C-NMR data were collected at room temperature on a Varian Gemini 200 spectrometer operating at 199.884 MHz for ^{1}H and at 50.27 MHz for ^{13}C with a 5-mm probe. NMR data were also obtained with a Bruker Avance spectrometer operating at 400.13 MHz for ^{1}H, at 100.56 MHz for ^{13}C, and at 128.377 MHz for ^{11}B. A 5-mm broadband probe was used, with the 90° pulse being 9 μs for ^{11}B and 7.5 μs for ^{13}C. The ^{11}B chemical shifts were reported with respect to 0.1M BA as an external reference. Chemical shifts for ^{1}H and ^{13}C were reported with respect to internal TMS, TSP, CDCl$_3$, or CH$_3$CN. To avoid any influence of the nuclear Overhauser effect (NOE), all ^{13}C spectra used for quantitative analysis were recorded with inverse-gated decoupling pulse sequences. In some cases, both proton-coupled and non-decoupled ^{13}C spectra were collected to aid in assignments. For the ^{11}B-NMR experiments, the samples were prepared by the dissolution of the appropriate amounts of BA and polymers in D$_2$O. In model compound experiments, 1:1 and 1:2 molar ratios of n-butylamine and glycidol, a 1:1 molar ratio of diethylamine and glycidol, and a 1:1 molar ratio of triethylamine and glycidol were combined with D$_2$O in 5-mm NMR tubes to form 1M solutions of the respective amines, and each reaction was followed overnight by ^{1}H-NMR.

Polymer titration

The pK_a values of the amine functionalities in the polymers were estimated by titration with 1.0N NaOH. Fifty milliliters of 1% polymer was adjusted to pH 2.0 with 1.0N HCl. The solution was titrated in 0.5 pH increments to pH 12.0 at room temperature. Because the moles of H$_3$O$^+$ and OH$^-$ present in the solution at low and high pH values were significant with respect to the number of moles of amines titrated, eq. (1) was used to calculate the moles of protonated amines titrated between each pH increment:

$$\Delta R_x H_y NH^+ = [OH^-]_t V_t + \{[H^+]_2 V_2 - [H^+]_1 V_1\}$$
$$- \{[OH^-]_2 V_2 - [OH^-]_1 V_1\} \quad (1)$$

where $\Delta R_x H_y NH^+$ is the change in the moles of protonated amines, $[OH^-]_t V_t$ is the total number of moles of the OH$^-$ titrant added, $\{[H^+]_2 V_2 - [H^+]_1 V_1\}$ is the number of moles of H$_3$O$^+$ neutralized, $\{[OH^-]_2 V_2 - [OH^-]_1 V_1\}$ is the number of moles of OH$^-$ of free base, V_t is the volume of the titrant used (L), V_1 is the volume at pH A (L), V_2 is the volume (L) of the solution at pH A + 0.5, $[H^+]_1$ is the hydronium ion concentration at V_1 (M), $[H^+]_2$ is the hydronium ion concentration at V_2 (M), $[OH^-]_t$ is the hydroxide concentration of the titrant (1.0N), $[OH^-]_1$ is the hydroxide ion concentration at V_1 (M), and $[OH^-]_2$ is the hydroxide ion concentration at V_2 (M). The activities were assumed to be equal to concentrations.

Boron-binding/retention studies

Solutions of PEI and the three functionalized derivatives of PEI were made at 1% polymer concentrations with the boron concentration ranging from 50 to 5000 ppm at room temperature. The pH values were measured, and 2-mL samples were ultrafiltered through 10,000 MWCO membranes with Centracon-10 units in a 20°C constant-temperature centrifuge; this yielded approximately 1 mL of permeate. Permeates were diluted and analyzed for the presence of boron by ICP–AES. The percentage of boron retained was determined by a linear standard curve of 1–50 ppm boron. Boron-binding/retention studies with the pH adjusted with HCl or NaOH were performed similarly, but the pH was adjusted volumetrically and recorded. Boron-binding studies in the presence of 0.1 and 0.5N NaCl were performed similarly, but 0.1 or 0.5N NaCl was added volumetrically, and the pH was recorded.

RESULTS AND DISCUSSION

Polymer preparation and characterization

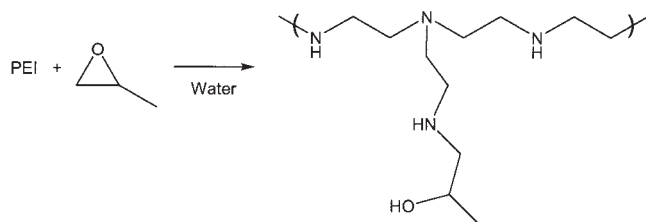Three derivatives of PEI containing functional groups with increasing numbers of linear, vicinal, hydroxy

Figure 1 Schematic of the method of preparation of monool-PEI.

groups per ARU attached mainly to the 1° amines were prepared: monool-PEI, 1,2-diol-PEI, and 1,2,3-triol-PEI. Monool-PEI and 1,2-diol-PEI were synthesized from commercially available propylene oxide and glycidol, respectively, as shown in Figures 1 and 2. The 1,2,3-triol-PEI was made from a ketal-protected butene oxide, as shown in Figure 3. The intermediates were purified by vacuum distillation and confirmed by IR and NMR spectroscopy. All the hydroxy polymers were formed by a *trans*-epoxide ring-opening reaction mainly with the 1° amines on the PEI backbone through the higher reaction rate with 1° amine sites (as discussed later) and the one-to-one molar ratio of oxirane to PEI. Monofunctionalization of the 1° amines served as a baseline for these types of simple functional groups by producing the lowest ARU MW (for these studies, ARU of PEI was designated to have the formula $C_8H_{20}N_4$).

The reactivities of *n*-butylamine, diethylamine, and triethylamine with glycidol in D_2O were examined to optimize the conditions for the synthesis of the PEI derivatives and to aid in their NMR spectroscopy characterization. In the equimolar mixture of *n*-butylamine with glycidol, it was observed by ^{1}H- and ^{13}C-NMR that about 20% of the 1° amines reacted with 2 equiv of glycidol to produce the disubstituted product bispropanediol butylamine, 60% were monosubstituted, and 20% did not react. In the 1:2 molar ratio with glycidol, about 15% of the *n*-butylamine reacted with one glycidol only; 85% was disubstituted. No evidence was seen for a trisubstituted amine. The reaction of equimolar glycidol with diethylamine in D_2O gave 72% of the monosubstituted product and 28% of the disubstituted quaternized product. The reaction of triethylamine with equimolar glycidol produced only 61% of the quaternized amine. The ^{1}H- and ^{13}C-NMR peaks due to glycidol disappeared completely in about 12 h for the reactions with triethylamine and diethylamine and in about 6 h for the reactions with *n*-butylamine. These results suggested that glycidol on a rate basis was most likely to react with the 1° amines of PEI; they also indicated that it was unlikely for quaternization to occur by a reaction with the tertiary (3°) amines in PEI as long as stoichiometric amounts of glycidol were used. A separate

NMR experiment showed that glycidol was stable in water for a period of 3 h; this demonstrated that water could be used as the solvent for these reactions.

^{13}C-NMR characterization

PEI and its hydroxy derivatives were characterized by ^{1}H- and ^{13}C-NMR spectroscopy to determine if the actual level of functionalization corresponded to the reaction stoichiometry and predicted reaction site preference. In the ^{1}H-NMR spectra at 400 MHz, all methylene signals resonated between δ values of 2.5 and 2.8 ppm; this made the assignment and quantitative analysis of CH_2 groups with different amine substituents very difficult. Therefore, ^{13}C-NMR spectra were analyzed, and most structural elements showed well-separated signals. Figure 4 shows the ^{13}C-NMR spectrum of PEI obtained with inverse-gated decoupling to avoid the influence of NOE on the signal intensities. The NMR spectrum shows characteristic signals for the CH_2 groups that were assigned according to previous works.[19,21,22] The ratio of 3°, 2°, and 1° amino groups in the polymer could be calculated from the signal integrals as follows:

$$1° : 2° : 3° = (A_7 + A_8) : (A_4 + A_5 + A_6)/2 : (A_1 + A_2 + A_3)/3 \quad (2)$$

This equation, applied to the NMR data, indicated that the PEI sample consisted of 35% primary amines, 34% secondary amines, and 31% tertiary amines. This is in agreement with the findings by von Harpe et al.[19] for commercially available PEI, even though this PEI was prepurified by diafiltration to retain only the MW fraction greater than 30,000 Da. These results are contrary to the manufacturer's (BASF) information and literature that specified a 1:2:1 molar ratio of 1°, 2°, and 3° amines.[23] The relative ratio of linear structures to branched structures, calculated from integrals of 2° amines to 3° amines, was 1.1; this indicated that, on average, every second amine formed a branch point. The branching of PEI causes its spherical-like structure for
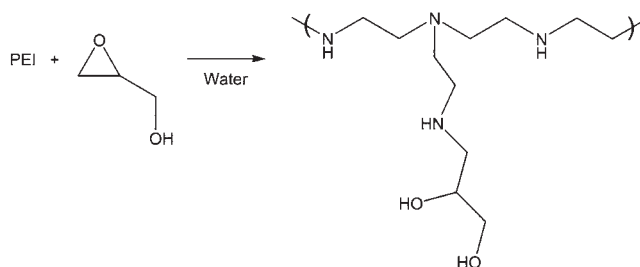

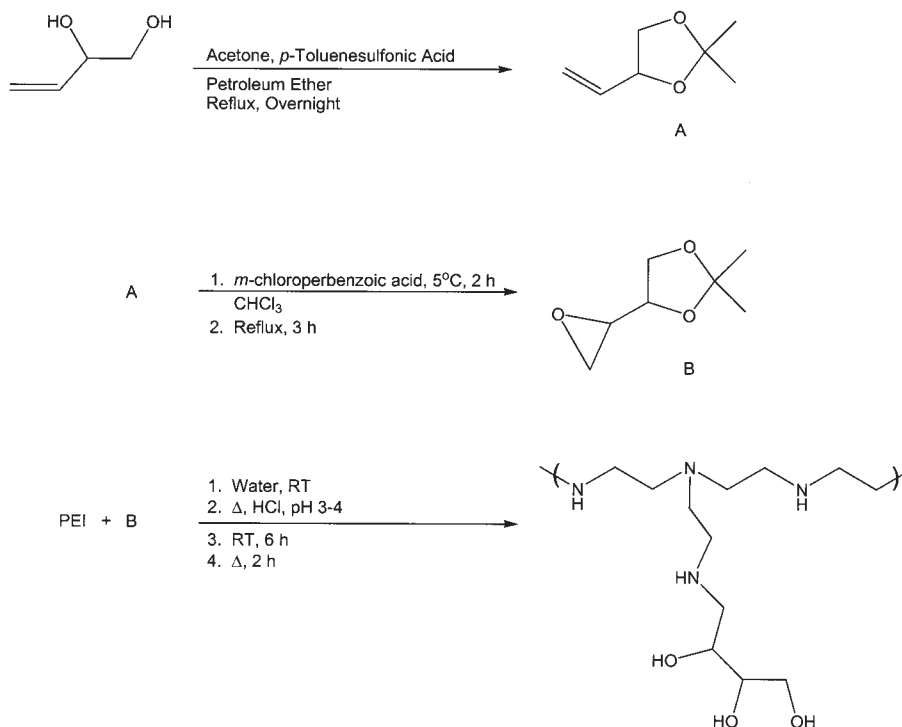**Figure 2** Schematic of the method of preparation of 1,2-diol-PEI.

Figure 3 Schematic of the synthesis of 1,2,3-triol-PEI.

low solution viscosities and makes it very useful in the PF process.

Figure 4 also shows ^{13}C-NMR spectra obtained for monool-PEI, 1,2-diol-PEI, and 1,2,3-triol-PEI. The chemical-shift assignments for these polymers are listed in detail in Table I. The ^{13}C-NMR spectrum obtained for the monool-PEI shows a total of nine large signals that were assigned as CH_2 groups (from 40 to 60 ppm), one broad signal associated with CH_3 groups (at ca. 23 ppm), and one large signal associated with CH groups (at ca. 69 ppm). Four smaller signals were observed for CH and CH_2 groups associated with monool substituents resulting from disubstitution of 1° amines of PEI and monosubstitution of 2° amines of PEI, as indicated in Table I for a', a'', b', and b''. The ^{13}C-NMR spectrum for the 1,2-diol displays CH_2 groups (from 40 to 60 ppm), CH_2 group nearest neighbors to OH groups (at ca. 67 ppm), and CH group nearest neighbors to OH groups (72–73 ppm). For the 1,2,3-triol-PEI, there was a set of signals associated with CH_2 groups (from 40 to 60 ppm), a set of signals associated with CH groups ranging from 72 to 77 ppm, and a set of signals associated with CH_2 group nearest neighbors to OH groups (at ca. 65 ppm). The integrals of the CH_2 groups of the PEI backbone of each of these polymers allow us to estimate the degree of branching and functionalization. Thus, the percentage of 3°, 2°, and 1° amines were 38, 43, and 19% for monool-PEI, 42, 40, and 18% for 1,2-diol-PEI, and 40, 45, and 16% for 1,2,3-triol-PEI, respectively. These results are listed in Table II.

When considering the 25% functionalization of these polymers (glycidol combined in a 1:4 molar ratio with total amines in the PEI ARU), we must discern
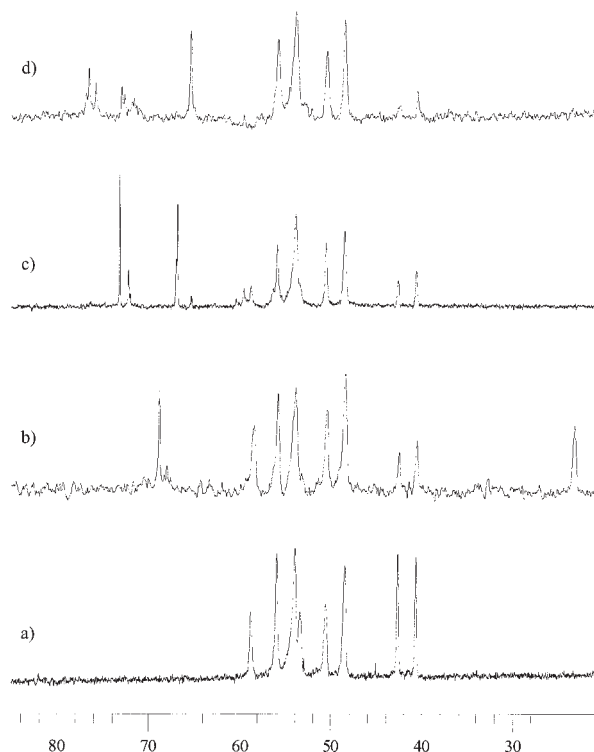

Figure 4 ^{13}C-NMR spectra (100.61 MHz, inverse-gated decoupled, 30°C) obtained in D_2O with TSP as a reference for (a) PEI, (b) monool-PEI, (c) 1,2-diol-PEI, and (d) 1,2,3-triol-PEI.

TABLE I
Inverse-Gated Decoupled ^{13}C 100.61-MHz NMR at 30°C

Carbon (Italicized) and abbreviation	PEI	Monool-PEI	1,2-Diol-PEI	1,2,3-Triol-PEI
NH$_2$CH$_2$CH$_2$NR$_2$, 8	40.6	40.6	40.6	40.5
NH$_2$CH$_2$CH$_2$NHR, 7	42.6	42.6	42.6	42.4
NHRCH$_2$CH$_2$NR$_2$, 6	48.4	48.5	48.5	48.4
NHRCH$_2$CH$_2$NHR, 5	50.5	50.5	50.5	50.4
NHRCH$_2$CH$_2$NH$_2$, 4	53.3	53.4	53.3	53.4
NRR'CH$_2$CH$_2$NR$_2$, 3	53.9	53.9	53.9	53.8
NRR'CH$_2$CH$_2$NHR, 2	55.9	55.9	55.9	55.8
NRR'CH$_2$CH$_2$NH$_2$, 1	58.8	58.8	58.7	58.2
NRHCH$_2$CH(OH)CH$_3$, a		58.5		
NR[CH$_2$CH(OH)CH$_3$]$_2$, a'		64.4		
NRR'CH$_2$CH(OH)CH$_3$, a''		63.4		
NRHCH$_2$CH(OH)CH$_3$, b		68.9		
NR[CH$_2$CH(OH)CH$_3$]$_2$, b'		68.2		
NRR'CH$_2$CH(OH)CH$_3$, b''		67.7		
NRHCH$_2$CH(OH)CH$_3$, c		23.2		
NR[CH$_2$CH(OH)CH$_3$]$_2$, c'		23.2		
NRR'CH$_2$CH(OH)CH$_3$, c''		23.2		
NRHCH$_2$CH(OH)CH$_2$(OH), d			56.3	
NR[CH$_2$CH(OH)CH$_2$(OH)]$_2$, d'			59.6	
NRR'CH$_2$CH(OH)CH$_2$(OH), d''			60.4	
NRHCH$_2$CH(OH)CH$_2$(OH), e			73.1	
NR[CH$_2$CH(OH)CH$_2$(OH)]$_2$, e'			72.2	
NRR'CH$_2$CH(OH)CH$_2$(OH), e''			71.9	
NRHCH$_2$CH(OH)CH$_2$(OH), f			66.8	
NR[CH$_2$CH(OH)CH$_2$(OH)]$_2$, f'			66.9	
NRR'CH$_2$CH(OH)CH$_2$(OH), f''			66.8	
NRHCH$_2$CH(OH)CH(OH)CH$_2$(OH)				Undiscernible
NR[CH$_2$CH(OH)CH(OH)CH$_2$(OH)]$_2$				Undiscernible
NRR'CH$_2$CH(OH)CH(OH)CH$_2$(OH)				Undiscernible
NRHCH$_2$CH(OH)CH(OH)CH$_2$(OH)				75.8
NR[CH$_2$CH(OH)CH(OH)CH$_2$(OH)]$_2$				72.9
NRR'CH$_2$CH(OH)CH(OH)CH$_2$(OH)				72.6
NRHCH$_2$CH(OH)CH(OH)CH$_2$(OH)				76.5
NR[CH$_2$CH(OH)CH(OH)CH$_2$(OH)]$_2$				76.9
NRR'CH$_2$CH(OH)CH(OH)CH$_2$(OH)				76.9
NRHCH$_2$CH(OH)CH(OH)CH$_2$(OH)				65.4
NR[CH$_2$CH(OH)CH(OH)CH$_2$(OH)]$_2$				65.4
NRR'CH$_2$CH(OH)CH(OH)CH$_2$(OH)				65.4

Chemical shifts [δ (ppm)] in D$_2$O with a TSP reference.

the proportion of 1°, 2°, and 3° amines of PEI that react with glycidol. No reaction of glycidol was observed with the 3° amines of PEI, in agreement with the considerably lower reactivity of 3° amines with glycidol for the model compound triethylamine. For 25% functionalized 1,2-diol-PEI, the somewhat well-separated resonances (e + e' + e'') of the CH(OH) group of the propyl diol substituents

TABLE II
Percentage of 1°, 2°, and 3° Amines for Purified PEI and Derivatives

Polymer name	3° : 2° : 1° (%)	3° : 2° : 1°
PEI	31 : 34 : 35	1.0 : 1.1 : 1.1
Monool-PEI 25% functionalized	38 : 43 : 19	2.0 : 2.2 : 1.0
1,2-diol-PEI 25% functionalized	42 : 40 : 18	2.3 : 2.2 : 1.0
1,2,3-triol-PEI 25% functionalized	40 : 45 : 16	2.5 : 2.9 : 1.0

resulting from monosubstitution and disubstitution of 1° amines of PEI (e + e', respectively) and from monosubstitution of 2° amines (e'') allow an estimate to be made of the relative ratios of each of these. An analysis of the ^{13}C-NMR integrals provides a reaction ratio of 67% for monosubstitution by glycidol of 1° amines of PEI, 28% for disubstitution of 1° amines, and 5% for monosubstitution of 2° amines. From the perspective of the amines bound to those carbons, this means that, of the total number of PEI amines that reacted with glycidol, 78% were 1° amines that monosubstituted, 16% were 1° amines that disubstituted, and 6% were 2° amines that monosubstituted. Thus, the polymeric structures shown in Figures 1–3 generally represent the overall polymeric product and indicate that through the direct reaction of PEI with oxiranes, the monosubstituted soluble polymers are the main reaction products.
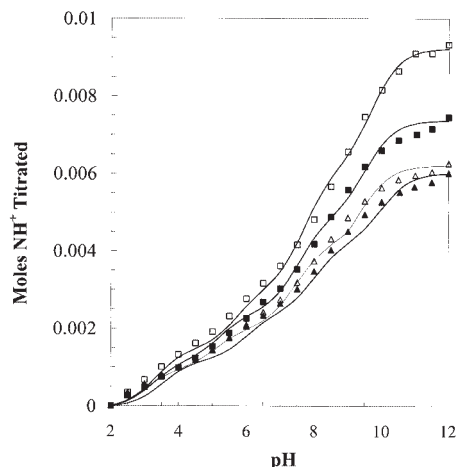
Figure 5 Polymer titration data obtained for PEI polymers: (□) PEI, (■) monool, (△) 1,2-diol, and (▲) 1,2,3-triol. The solid curves represent a fit of the data.
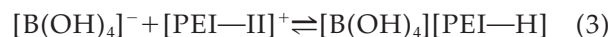
Polyamine characterization

Solutions of the polymers were made acidic (pH 2) and titrated with dilute base to determine the average pK_a values of the functionalized polymers in comparison with that of PEI. The moles of protonated amines titrated over each pH increment were summed to yield graphs that represent moles of protonated amines titrated versus the pH (see Fig. 5). For all four polymers, only about 75% of the amines were protonated at pH 2.0 (see Table III). This effect can be explained by strong nearest neighbor interactions of charged groups along the branched polymer chain, and this has also been reported to affect the pK_a values of the amines as the degree of amine protonation increases.[23,24]

Attempts to empirically fit the titration data indicated that a reasonable fit could be achieved by the assumption of the presence of amine sites with four different pK_a values. The results of these fits are represented as solid curves in Figure 5. The pK_a values and ARU fractions for the amines used to fit the titration data are presented in Table III. These results show that at pH 2.0, PEI, monool-PEI, and 1,2-diol-PEI had 3.0 mol of protonated amines/ARU, whereas 1,2,3-

triol-PEI had 3.30 mol of protonated amines/ARU. The pK_a values of the functionalized polymers were quite similar to the value for PEI, indicating that functionalization of PEI with hydroxyl groups did not significantly change the hydrophobicity and basicity of PEI. If functionalization had changed the hydrophobicity, considerably lower pK_a values would have been expected with respect to that of PEI.[23] At near neutral pH values, all the polymers had about 1.6–1.8 mol of protonated amine/ARU, and this indicated that the polymers could act as weak base anion exchangers even at nearly neutral to slightly basic pH values. The amine-containing polymers could behave as proton sinks, providing buffering capability, and could enhance the stability of borate esters.[25]

Boron-binding studies

There are essentially two binding mechanisms through which BA/borate can interact with the functionalized polymers: ion pairing and borate ester formation. The ion pairing occurs between the borate anion and the weak base anion-exchange site as follows:

$$[B(OH)_4]^- + [PEI\!-\!II]^+ \rightleftharpoons [B(OH)_4][PEI\!-\!H] \quad (3)$$

The second boron-binding mechanism occurs through borate ester formation either as a borate monoester [Fig. 6(a)] or as borate diesters [Fig. 6(b,c)]. ^{13}C-NMR characterization indicated that only 16% of the amine sites in the 1,2-diol-PEI were disubstituted, and this suggests that only small amounts of the compound [Fig. 6(c)] are formed; thus, its overall contribution to boron binding should be less significant, except possibly at very low boron concentrations.

A critical issue for boron binding is the configuration of the vicinal hydroxy groups. The 1,2-diol-PEI polymer is composed of a terminal 1,2-diol, whereas the 1,2,3-triol-PEI polymer has a terminal 1,2-diol, either a 1,2-*threo*- or 1,2-*erythro*-diol, and a 1,3-diol configuration. The terminal hydroxy of the 1,2-diol can rotate to form a *cis*-diol configuration, which can then react with borate to form borate monoesters. The con-

TABLE III
ARU Fractions and pK_a Values Obtained for PEI and Derivatives

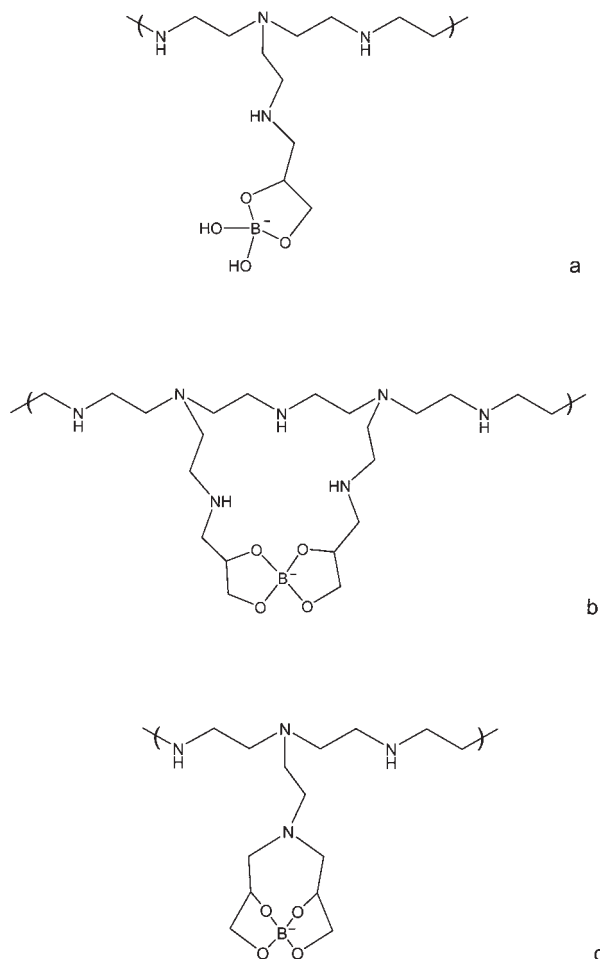| Protonated Amine	PEI		Monool		1,2-Diol		1,2,3-Triol	
	pK_a	ARU fraction	pK_a	ARU fraction	pK_a	ARU fraction	pK_a	ARU fraction
First amine	3.30	0.5	3.22	0.5	3.00	0.5	3.52	0.67
Second amine	5.70	0.5	5.22	0.5	5.10	0.5	6.00	0.67
Third amine	7.70	1.0	7.52	1.0	7.40	1.0	8.00	1.00
Fourth amine	9.70	1.0	9.52	1.0	9.46	1.0	10.00	1.00
Total protonated amines/ARU	—	3.0	—	3.0	—	3.0	—	3.33

Figure 6 Formation of (a) borate monoester and (b,c) borate diesters in the water-soluble 1,2-diol-PEI polymer.

figuration of the hydroxy group formed upon the opening of the oxirane ring is an important factor in the formation of borate esters in 1,2,3-triol-PEI. The terminal vicinal diol portion of the functional group is fixed in the cis configuration as a ketal. The trans ring-opening reaction gives rise to a 1 : 1 mixture of threo and erythro for the second 1,2-diol configuration.[26] The stability order of vicinal diols is expected to increase as $K_{\text{threo}} > K_{\text{terminal}} > K_{\text{erythro}}$.[16] Statistically, we anticipate that the boron-binding constant for the 1,2,3-triol-PEI will be larger than that for 1,2-diol-PEI because of a larger number of vicinal hydroxy groups.[16] However, the geometry of the third hydroxy groups in 1,2,3-triol-PEI is such that only half of the OH groups are configured in the correct geometry (threo) for optimum binding. In the case of monool-PEI, boron binding might be relatively weak because ester formation with a single hydroxy group is expected to be unstable in aqueous media but could potentially be stabilized through ester formation on multiple sites within a polymeric matrix.[16] Boron-binding experiments were performed both with and without pH adjustment. When the pH of the solution was not adjusted, it simulated the conditions that would occur if the polymer were added to water removed from the primary coolant loop in a PWR, for which BA (1–1000 ppm) dissolved in high-purity water is the major constituent. In these systems, there are no constituents other than small quantities of ^{7}LiOH and trace constituents originating from system corrosion, activation, and fission products. In a second set of experiments, the pH was adjusted to evaluate its effect on BA binding.

Boron-binding studies: No pH adjustment

The amine backbone of the PEI polymer buffers the BA, and this results in a range of pH values as BA is mixed with the soluble polymer in different proportions. For example, the pH was determined to vary from 9.74 to 5.71 for a fixed 1% solution of the 1,2-diol-PEI while the boron concentration changed from 57 to 8700 ppm, as shown in Figure 7.

The observed pH is dependent on the equilibrium constants for the amines making up the backbone of the polymer and BA as follows:

$$\frac{[\text{H}^+][\text{R}_x\text{H}_y\text{N}]}{[\text{R}_x\text{H}_y\text{NH}^+]} = K_a$$

$$\frac{[\text{H}^+][\text{B(OH)}_4{}^-]}{[\text{H}_3\text{BO}_3]} = K$$

where $\text{R}_x\text{H}_y\text{N}$ refers to the 1°, 2°, and 3° amines that make up the polymer backbone.

Boron-binding experiments were performed for the three functionalized polymers and PEI. The polymer concentration was kept constant at 1% as the boron
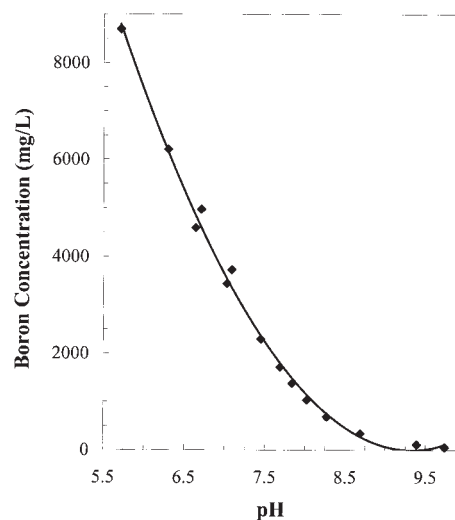

Figure 7 BA concentration versus the pH in 1% 1,2-diol-PEI polymer (the solid line is a trend line).
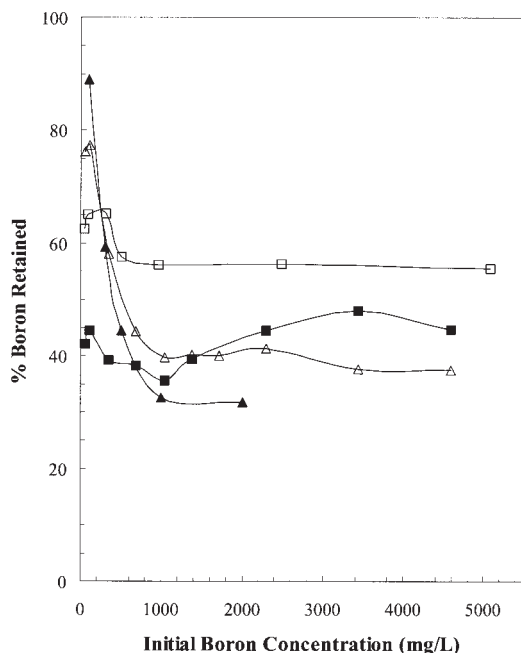
Figure 8 Percentage of boron retained as a function of the initial boron concentration: (□) PEI, (■) monool-PEI, (△) 1,2-diol, and (▲) 1,2,3-triol.

Figure 10 1,2-Diol-PEI binding (1%) as a function of the boron concentration at 20°C. The pH was not adjusted.

concentrations were varied, and the pH values were recorded. Figures 8 and 9 show the percentage of boron retained during UF for PEI and its hydroxy derivatives as a function of the boron concentration and pH, respectively. The amount of boron retained for PEI was between 55 and 65%, regardless of the pH
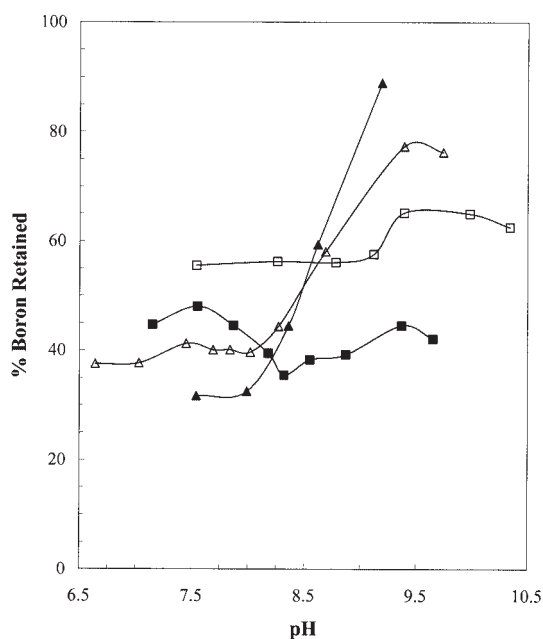

Figure 9 Percentage of boron retained as a function of pH: (□) PEI, (■) monool-PEI, (△) 1,2-diol, and (▲) 1,2,3-triol.
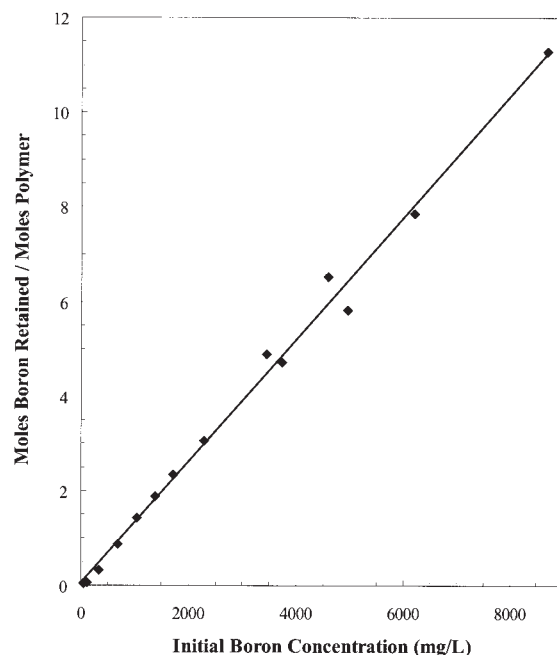
or boron concentration. Monool-PEI showed boron-binding behavior similar to that observed for PEI; that is, the amount of boron that was retained (40–50%) remained relatively constant over a large boron concentration range. The boron-binding results for 1,2-diol-PEI have a different profile than those observed for PEI and monool-PEI. At low boron concentrations (higher pH), a much larger percentage of the total boron was retained. The total amount of boron retained decreased from 78% at about 100 mg/L boron and pH 9.5 to a constant value of about 40% at boron concentrations of 700 mg/L and higher pHs (6.5–8). The results for 1,2,3-triol-PEI show a profile similar to that observed for 1,2-diol-PEI, except that 1,2,3-triol-PEI exhibited a higher level of boron retention (90%) at low boron concentrations (100 mg/L). At higher boron concentrations (>1000 mg/L), a leveling in the retention percentage similar to that of 1,2-diol-PEI can be observed; however, it plateaus at a 30% retention percentage versus 40% for 1,2-diol-PEI.

Experiments were performed to examine the binding capacity of 1,2-diol-PEI. A plot of the moles of boron retained per ARU as a function of the initial boron concentration within the range of 100–10,000 mg/L boron for 1,2-diol-PEI is shown in Figure 10. This plot indicates that the moles of boron retained increased linearly as the initial boron concentration increased. At an initial boron concentration of approximately 5000 mg/L, 6 mol of boron/ARU was retained. As the boron concentration was increased to about 9000 mg/L, 11.3 mol of boron/ARU was retained. This number far exceeds the 1,2-diol-PEI ca-

pacity for ester formation, which is estimated to be only 1 mol of boron/ARU.

These results indicate that PF has the potential to recover very high concentrations of BA for PWR applications, even though PF technology is usually applied for dilute solute recovery.[8] The moles of boron recovered per ARU considerably exceeded the expected capacity of the 1,2-diol functional group; thus, we infer that boron binds to the polymer not only by borate ester formation but also through ion pairing with the protonated amines. If one considers both mechanisms for boron binding and a stoichiometric ratio of 1:1, the maximum possible boron retention capacity, under the assumption that all amines can be protonated, is 5 mol of boron/ARU because the repeat unit contains four amines (ion pairing) and one 1,2-diol group (borate monoester formation). This value is well below the value of 11.3 observed for 9000 mg/L boron. The additional retention capacity can be explained by the formation and binding of polyborate species, which are known to form at high BA concentrations.[27,28] This observation puts into question capacity data for any amine-containing diol or polyol presented in the literature that were determined at only one initial boron concentration in the absence of an ionic strength adjustment.

Boron-binding studies: pH adjusted

A set of experiments was performed for the three functionalized polymers plus the PEI backbone at a constant polymer concentration of 1% and a fixed
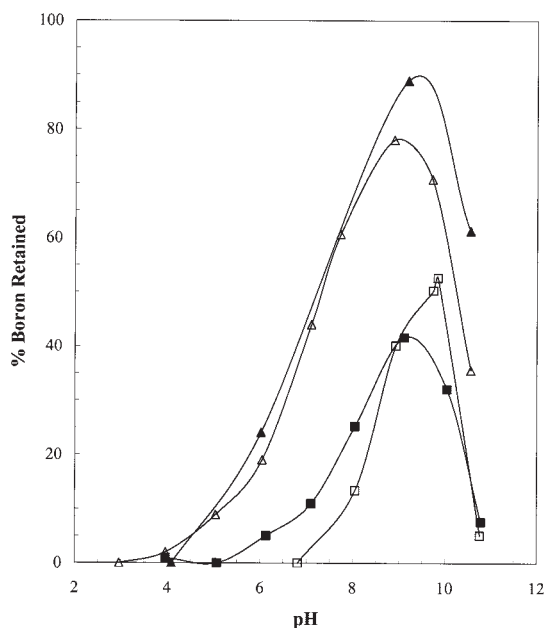

Figure 11 Retention curves as a function of pH at 100 mg/L boron for (□) PEI polymer, (△) 1,2-diol-PEI, (■) monool-PEI, and (▲) 1,2,3-triol-PEI.
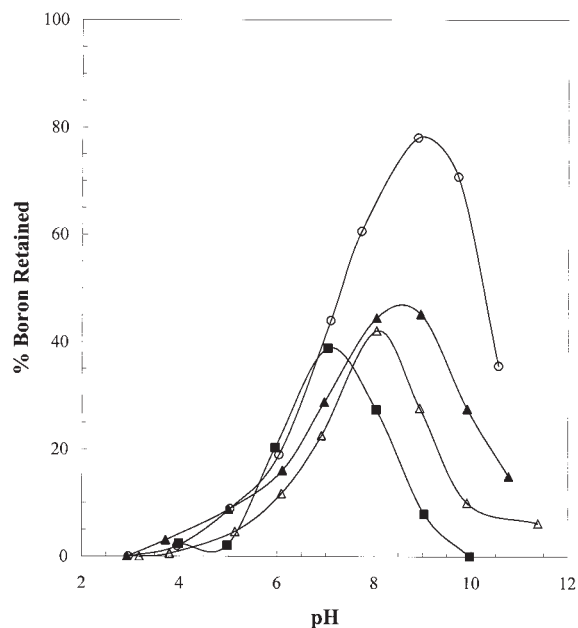

Figure 12 Percentage of boron retained as a function of pH for 1% 1,2-diol-PEI and initial boron concentrations of (○) 100, (▲) 500, (△) 1000, and (■) 5000 mg/L.

boron concentration of 100 mg/L. The pH was adjusted with HCl and NaOH. The percentages of boron retained as a function of pH are illustrated in Figure 11. The data indicate that the amount of boron retained varied according to the polymer: 1,2,3-triol-PEI > 1,2-diol-PEI > PEI ≅ monool-PEI. The maximum boron retention occurred before acid or base was added to the solution. For all four polymers, the addition of acid or base resulted in a decrease in the total amount of boron retained. To investigate these findings in more detail, we performed the same set of experiments for 1,2-diol-PEI as a function of several initial boron concentrations, instead of just 100 mg/L, as shown in Figure 12. The same effect was observed; that is, the percentage of boron retained decreased each time that the pH of the solution was adjusted. We infer that the maxima of the retention plots shown in Figures 11 and 12 are partly due to ion pairing, in which boron was ion-paired with a protonated amine $\{[R_x H_y NH^+ \text{ and } B(OH)_4^-]\}$. As the pH of the solution increases, the amines become less protonated, and this reduces ion pairing to boron. As the pH of the solution is lowered, the borate/BA equilibrium is shifted; this results in a decrease in the total borate ion concentration, and this also decreases the formation of ion pairs. In addition, the pH adjustment increases the ionic strength of the solutions, and this may suppress ion pairing.

Salt suppression studies

A significant fraction of boron appears to interact with the polymers by means of ion pairing. This effect

TABLE IV
Percentage of Boron Retained for PEI and Derivatives as a Function of Boron and NaCl Concentrations

| | Retention (%) | | | | | |
| | 100 mg/L B | | | 1000 mg/L B | | |
Polymer	Without NaCl	0.1M NaCl	0.5M NaCl	Without NaCl	0.1M NaCl	0.5M NaCl
PEI	65.0	0	0	56.1	10.4	5.5
Monool	44.5	2.0	0	35.5	14.5	2.9
1,2-Diol	77.3	43.2	16.1	39.7	11.9	5.1
1,2,3-Triol	88.7	76.4	80.2	32.5	24.8	22.2

renders more difficult the task of evaluating the effectiveness of the hydroxy groups in forming borate esters. However, the addition of a salt such as sodium chloride is expected to suppress the ion-pairing effect with little effect on borate ester formation, making it possible to assess the importance of the hydroxy groups for borate ester formation.[28] To evaluate this concept, salt suppression studies were performed with 0.1 and 0.5M sodium chloride concentrations and a fixed 1% polymer concentration. Two representative and relevant boron concentrations were chosen, 100 and 1000 mg/L, and the pH of the solutions was not adjusted. The results reported in Table IV show that the percentage of retained boron decreased substantially as salt was added to the solutions. This effect was observed for three of the four polymers at both boron concentrations. This result alone indicates the presence of significant ion pairing in these systems. The amount of salt required to suppress ion pairing can be estimated from the retention data obtained for PEI, as ion pairing is the only means of boron binding with PEI. Because a boron concentration of 100 mg/L is about 0.01M, this corresponds to a chloride/boron ratio of approximately 10 for 0.1M salt and 50 for 0.5M salt. For a boron concentration of 1000 mg/L, chloride/boron ratios are approximately 1 for 0.1M salt and 5 for 0.5M salt. Consequently, we estimate that to suppress the ion-pairing effect of PEI, a chloride/boron ratio of about 10 is needed. Below this ratio, we expect ion pairing to take place. For the solution of monool-PEI and 100 mg/L boron, there was essentially no boron retained when salt was added. This result corroborates the retention studies indicating that this polymer does not form any borate esters; boron binding occurs only through the ion-pairing mechanism. For the 1,2-diol-PEI and 100 mg/L boron concentration, almost half (43%) of the boron was retained when salt was added to the solution. For 1,2,3-triol and the same boron concentration, an even larger percentage (76%) of boron was retained when salt was added to the solution. These results indicate that boron interacts with these two polymers by means of ion pairing and also through borate ester formation. Of these two polymers, 1,2,3-triol-PEI has the highest percentage of ester formation.

Retention experiments were performed with 1,2-diol-PEI through variations in the boron concentrations in a 0.1M NaCl solution, as shown in Figure 13. Although the salt concentration was not high enough to completely suppress ion pairing at the higher boron concentrations, the graph indicates an increased percentage of ester formation at the lower boron concentrations or when the boron-to-functional-group ratios are smaller, as previously observed.[13]

Salt suppression by 0.1M NaCl eliminates the ion pairing observed for PEI. If the values for the retention percentage from the 0.1M NaCl suppression studies for 1,2-diol-PEI and 1,2,3-triol-PEI at a 100 mg/L boron concentration represent ester formation without a significant contribution from ion pairing, an overall formation constant (K_d) for 1,2-diol and 1,2,3-triol can be calculated:
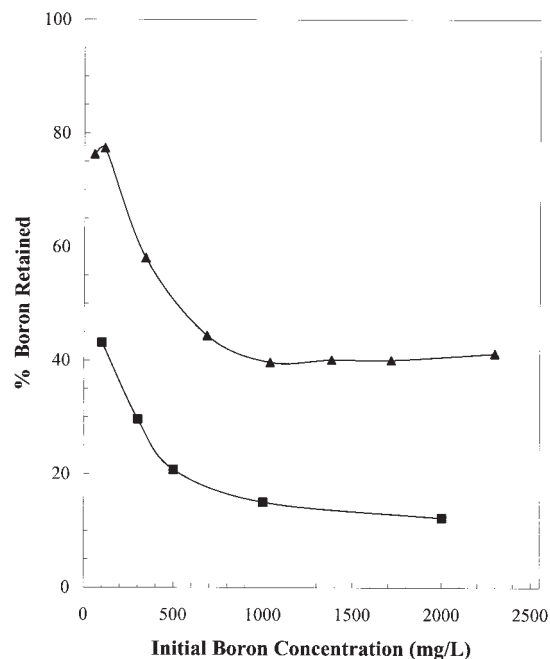
$$K_d = \frac{[BL]}{[B][L]}$$

Figure 13 Boron concentration versus the percentage of boron retention for 1% 1,2-diol-PEI: (■) with and (▲) without 0.1 M NaCl.

TABLE V
Calculated Formation Constants for 1% 1,2-Diol-PEI and
1,2,3-Triol-PEI with 100 mg/L Boron and 0.1M NaCl

Polymer	Retention (%)	pH	K_d
1,2-Diol-PEI	43.2	9.87	21
1,2,3-Triol-PEI	76.4	9.30	111

where B is the free boron concentration (M), L is the free ligand concentration (M; based on ARU molarity), and BL is the boron ester (M). Table V lists the calculated K_d values for the 1,2-diol and 1,2,3-triol polymers. The data indicate that the 1,2,3-triol polymer has a substantially higher boron ester formation constant than the 1,2-diol polymer. However, when one considers both ion pairing and ester formation, the total boron retention capabilities of the two polymers on a mass basis are similar (77% for the 1,2-diol and 89% for the 1,2,3-triol).

^{11}B-NMR characterization

Because salt suppression does not discriminate between borate monoester and borate diester forma-

tion, ^{11}B-NMR experiments were performed to detect and confirm ester formation for the polymers under investigation. ^{11}B-NMR spectroscopy has been used as a powerful tool to study the structure of borate complexes of sugars and alcohols.[16,25] The ^{11}B-NMR spectra at room temperature for 1% solutions of PEI and derivatives with 0.05M BA are shown in Figure 14. The complexation between BA/borate and 1,2-diol sites is slow with respect to the ^{11}B-NMR timescale, and so signals due to the ester complexes are observed separately from those of BA/borate. The chemical shift of the BA/borate signal is a function of the solution pH and is indicative of the amount of borate ion present in the solution. For instance, the chemical shift is close to −17.7 ppm at pH 11, at which borate ions predominate in the solution.[29] For 1,2-diol- and 1,2,3-triol-PEI polymers, three peaks can be observed in the spectrum: BA/borate (−2.9 ppm), monoester (−13.7 ppm), and diester (−9.8 ppm). For PEI, only one peak at −7.4 ppm was detected. This peak was assigned to the BA/borate species, whose relatively high negative shift is associated with the higher pH of PEI with respect to that of the functionalized derivatives. These chemical shifts indicate that the
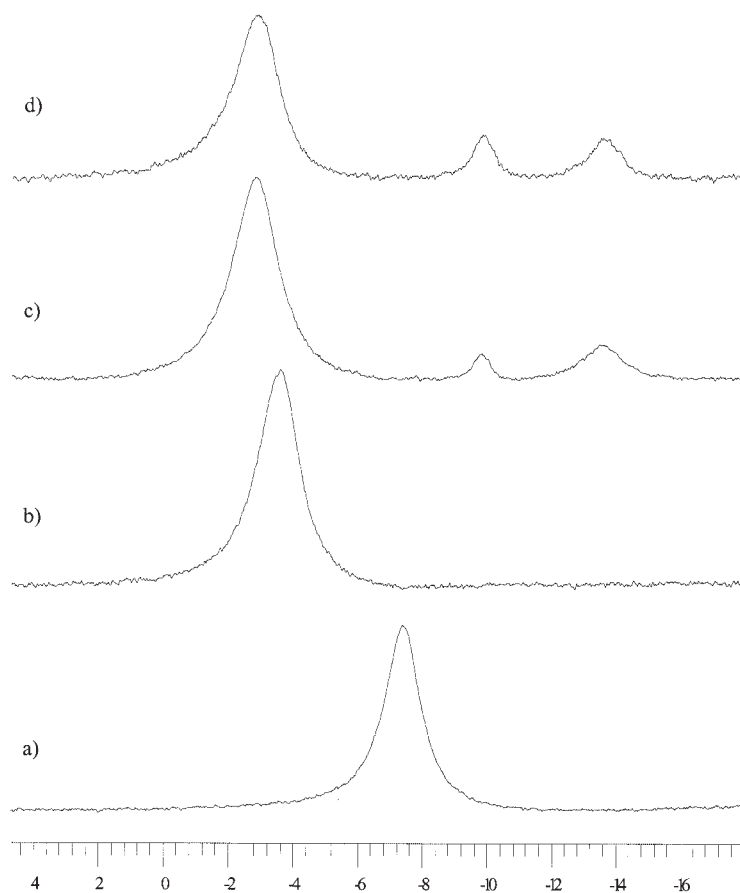

Figure 14   ^{11}B-NMR spectra for (a) PEI, (b) monool-PEI, (c) 1,2-diol-PEI, and (d) 1,2,3-triol-PEI.

functionalized polymers on a 1% weight basis are slightly less basic than PEI.

For the monool-PEI sample, the ^{11}B-NMR spectrum is very similar to the one obtained for PEI, showing only one peak at −3.6 ppm. No borate ester complexes were detected for the monool-PEI, and this indicates that even the close proximity of hydroxy groups on different branches of the polymer backbone was not enough to stabilize ester formation. For both 1,2-diol- and 1,2,3-triol-PEI, we observe in the ^{11}B-NMR spectra more borate monoester than diester species, and this is what has been reported in the literature for similar functional groups at higher boron-to-functional-group ratios.[13,16] This result is reasonable because the amines of the PEI derivatives are mainly monosubstituted (84% of the amines in 1,2-diol-PEI). When the binding constant of the hydroxy group is high enough to yield high retention values with only borate monoester formation, that results in a higher overall polymer boron capacity (i.e., one boron per binding per site vs one boron per two hydroxyl binding sites). For a diester to form, boron must bind intramolecularly to another 1,2-diol group on an adjacent branch, intermolecularly between two macromolecules, or intramolecularly with a disubstituted amine (16% of the amines in 1,2-diol-PEI; see the structures in Fig. 6). The 1,2,3-triol-PEI has larger relative peak areas for the borate esters than the 1,2-diol-PEI, and this indicates that overall the 1,2,3-triol-PEI is a better chelator than the 1,2-diol. This is in agreement with boron-binding studies, which indicate that increasing the number of vicinal hydroxyl functional groups increases their ability to bind boron.[16]

At low boron concentrations, 1,2,3-triol-PEI performs better than 1,2-diol-PEI. If these two polymers are compared on a constant molar basis instead of a constant weight-per-volume basis, the difference between the two is more pronounced. For example, the boron removal at 100 ppm would be 99.5% for 1,2,3-triol-PEI and only 77.3% for 1,2-diol-PEI on a molar basis. In contrast, boron binding of 1,2,3-triol-PEI at a higher boron concentration (1000 ppm) was less than that for 1,2-diol-PEI on a weight-per-volume basis as well as a molar weight basis.

The data obtained in this study provide important information for designing boron-selective functional groups and about the interaction between boron species and functional groups in future polymers. One consideration that arises when we compare 1,2-diol-PEI and 1,2,3-triol-PEI for a possible boron separation process spanning a concentration range of 1–1000 ppm boron is whether the more involved multistep preparation of 1,2,3-triol-PEI (vs the single-step preparation of 1,2-diol-PEI) is commensurate with its somewhat higher level of boron recovery at lower boron concentrations. Senkal and Bicak's[17] results with a crosslinked methacrylate polymer functionalized with iminodipropylene glycol suggest that improved performance might be achieved by an increase in the level of functionalization of PEI with 1,2-diols from 25% to a higher value to improve boron retention, instead of preparing functional groups for PEI with more linear hydroxy groups (e.g., 1,2,3,4-tetraol).[7] Preliminary data from our laboratory have been obtained and will be reported later.

The facile reversal of boron binding is an important factor for recycling EBA in the nuclear power industry. The temperature reversal of boron binding is more amenable to nuclear power applications than the more often reported acid or base stripping.[13,17] Preliminary ^{11}B-NMR results indicate that an increase in temperature to 80°C suppresses borate ester formation for 1,2-diol-PEI. The binding of borates with anion-exchange resins through ion pairing has been reported to decrease as temperature rises.[30] The ability of these water-soluble polymers to act as temperature-reversible boron chelators is under current investigation.

CONCLUSIONS

We have synthesized and fully characterized new water-soluble PEI polymers containing three different linear alkyl alcohol ligands: monool, 1,2-diol, and 1,2,3-triol. These polymers were especially designed to be used for boron removal and recycling in polymer-assisted UF technology. The studies reported in this work have demonstrated the high boron removal capacity of 1,2-diol and 1,2,3-triol. At an equal polymer concentration of 1%, the 1,2,3-triol polymer outperformed the 1,2-diol at low boron concentrations, but the 1,2-diol-PEI polymer outperformed the 1,2,3-triol-PEI at high boron concentrations. We have also determined that boron binds to these polymers through borate ester formation and through ion pairing with the protonated amines. We have demonstrated that ion pairing is the only means for boron binding in monool-PEI and PEI.

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