

Boric Acid Binding Studies with Diol Containing Polyethylenimines as Determined by ^{11}B NMR Spectroscopy

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ABSTRACT: Three water-soluble polymers incorporating increasing levels of 2,3-dihydroxy propyl attached to polyethylenimine (PEI) backbone were synthesized, characterized by NMR, and investigated for their ability to bind boric acid (BA). ^{11}B NMR spectroscopy showed that BA interacted with the polymeric 2,3-dihydroxy propyls by forming borate monoester and borate diesters in the boron concentration range of 100–1000 ppm and at 0.0775M polymer. Borate monoester species predominated for low functionalization levels (33% of the PEI amines functionalized), whereas borate diester species dominated for the higher functionalized polymers (66–100% of the PEI amines functionalized). All three polymers showed that 100% of the BA was bound as a mixture of borate mono- and diesters

at 100-ppm boron. The overall best performer based on total borate ester formation was the 2/3-PEI, with a binding K_d of 631 at 200 ppm boron. Borate ion concentration was measured from the ^{11}B NMR chemical shift of the BA/borate peak and it decreased as 1/3-PEI > 2/3-PEI > 3/3-PEI. Variable temperature ^{11}B NMR showed drastic reduction of borate ester species at 65°C. Thus, PEI polymers, as the ones investigated in this work, are reasonable candidates for the selective recovery and recycle of BA. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4411–4418, 2006

Key words: water-soluble polymers; ^{11}B NMR; polyethylenimine; boric acid; diol

INTRODUCTION

We are interested in developing and optimizing water-soluble polymers for polymer-assisted ultrafiltration technology as a method to concentrate, recover, and recycle boric acid (BA). BA is used in the nuclear power industry as an adjustable neutron-absorbing additive in the primary coolant water of pressurized water reactors (PWRs).¹ The use of ^{10}B -enriched BA has been proposed as a way to (i) increase fuel cycles and fuel burn-ups, and (ii) to reduce the required concentration of BA, which is associated with stress corrosion cracking in the primary coolant loop and Zircaloy fuel-cladding corrosion.^{2,3} Recent studies⁴ performed by our group have shown that polyethylenimine (PEI) functionalized with 2,3-dihydroxy propyls are efficient polymer systems to recover BA because (i) they have a low average-repeat-unit (ARU) molecular weight (MW), (ii) they provide sufficiently stable boron adducts, and (iii) they are easy to synthesize.

In the present work, we report the synthesis and characterization of three levels of functionalized 2,3-dihydroxy propyl-PEI polymers. The polymers were prepared by functionalizing the primary and secondary amines on the PEI backbone by attaching hydroxyl functional groups through an oxirane ring-opening reaction. The degree of functionalization was estimated from ^{13}C NMR experiments. We made use of ^{11}B NMR spectroscopy to assess boron-binding properties of the 2,3-dihydroxy propyl-PEI polymers over a wide boron concentration and temperature range to predict polymer performance in actual ultrafiltration processes. ^{11}B NMR spectroscopy has been widely employed to identify borate esters of hydroxyl compounds in aqueous solution,^{5,6} providing an excellent tool for the quantitative determination and structure elucidation of esters in aqueous medium.

EXPERIMENTAL

Chemicals

Glycidol (96%) [Aldrich] was freshly vacuum-distilled before use. NMR solvents and standards [Aldrich, Milwaukee, WI]: D_2O (99.9 atom % D), 3-(trimethylsilyl) propionic-2,2,3,3- d_4 acid sodium salt (TSP-98 atom % D); boric acid [Baker-analyzed, Phillipsburg,

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TABLE I
Amounts of Starting Materials Used to Synthesize 2,3-Dihydroxy Propyl PEI Polymers

2,3-Dihydroxy propyl PEI	Glycidol (g)	Glycidol (mol)	10.3% w/v PEI solution (mL)	PEI (g)	ARU MW (g)
1/3-PEI	5.90	0.0797	100	10.3	203
2/3-PEI	11.80	0.1594	100	10.3	277
3/3-PEI	17.71	0.2391	100	10.3	351

NJ], NaCl (Fisher ACS-certified, Fair Lawn, NJ), and buffers of pH 4.00, 7.00, and 10.00 [Fisher] were used as received.

Equipment

Instruments and equipment used included an analytical balance (Mettler, Model AC 100), freeze dryer (Labconoco, Model Freezone 4.5), evaporator (Buchi, RE 120), autopipets (Rainin electronic digital pipettes: 10.00 mL, 2.500 mL, 250.00 μ L, and 25.00 μ L), pH meter (Orion Model 210A; Orion Model 520A; Orion Ross L Combination Model 81-C2 pH electrode), stirrer/hotplate (Corning), deionized (DI) water purifiers (Culligan; Barnstead e-pure; with a minimum resistivity of 17.5 M Ω cm at 25 $^{\circ}$ C).

Preparation of 2,3-dihydroxy propyl-PEI polymers

The preparation of PEI was reported in a previous study.⁴ The structure of PEI was calculated as a three-nitrogen-containing ARU with a MW of 129 g/mol and a repeat unit formula of C₆H₁₅N₃, based on the determination that purified PEI consisted of 1 : 1 : 1 ratio of 1 $^{\circ}$: 2 $^{\circ}$: 3 $^{\circ}$ amines.⁴ Glycidol was added to a 10.3% w/v aqueous PEI solution (100 mL) in a 250-mL round bottom flask over a 10-min period at room temperature (see Table I for proportions). The solution was stirred overnight at room temperature and then heated to near reflux for 2 h. The cooled solution was diafiltered through a 30,000 MWCO membrane with 5–6 volume equivalents of DI water.⁷ The product concentrate was frozen with liquid N₂ and placed on a freeze dryer overnight to remove water, giving a solid, glassy product in nearly quantitative yield. The samples for ¹¹B NMR studies were prepared by dissolution of the appropriate amounts of BA and polymers in D₂O. Stock solutions of PEI and the three 2,3-dihydroxy propyl-PEI polymers were prepared and mixed with 10,000 ppm B stock solution to give 0.0775M polymer concentrations (1% w/v PEI is 0.0775M) with boron ranging from 100 to 9000 ppm and brought to volume with D₂O. The pD values were measured at room temperature (25 $^{\circ}$ C) for each sample. The pH electrode was calibrated at 25 $^{\circ}$ C with pH 4.00, 7.00, and 10.00 buffer solutions (pD = pH + 0.4). Samples with NaCl were performed similarly, where

stock 4M NaCl or solid NaCl was added to obtain the desired salt concentration and the pD was recorded at room temperature (25 $^{\circ}$ C). The effect of salt concentration on pD was determined for PEI in the presence and absence of BA, and for BA alone.

¹H NMR data (400.13 MHz, D₂O): for 1/3-diol-PEI: 2.6–3.0 (13H, CH₂), 3.5–3.7 (2H, m, CH₂OH), 3.8–4.0 ppm (1H, CH(OH)); for 2/3-diol-PEI: 2.6–3.0 (7H, CH₂), 3.5–3.7 (2H, m, CH₂OH), 3.8–4.0 ppm (1H, CH(OH)); for 3/3-diol-PEI: 2.6–3.0 (5H, CH₂), 3.5–3.7 (2H, m, CH₂OH), 3.8–4.0 ppm (1H, CH(OH)).

NMR measurements

NMR data were collected on a Bruker Avance spectrometer operating at 400.13 MHz for ¹H, 100.56 MHz for ¹³C, and 128.377 MHz for ¹¹B. A 5 mm broadband probe was used with the 90 $^{\circ}$ pulse being 9 μ s for ¹¹B, 7.5 μ s for ¹³C, and 8.2 μ s for ¹H. The ¹¹B chemical shifts were reported with respect to 0.1M BA as an external reference. NMR quartz tubes from Aldrich were used for ¹¹B NMR experiments. Chemical shifts for ¹H and ¹³C were reported relative to internal TSP. To avoid any influence of the nuclear overhauser effect (NOE), all ¹³C spectra used for quantitative analysis were recorded using inverse-gated decoupling pulse sequences.

RESULTS AND DISCUSSION

¹³C NMR characterization

Three water-soluble polymers with increasing amounts of 2,3-dihydroxy propyl functionality attached to the amino groups of PEI were prepared: 1/3, 2/3, and 3/3-PEI (the nomenclature derived from the ratio of amines to reacted glycidol). These ratios were chosen

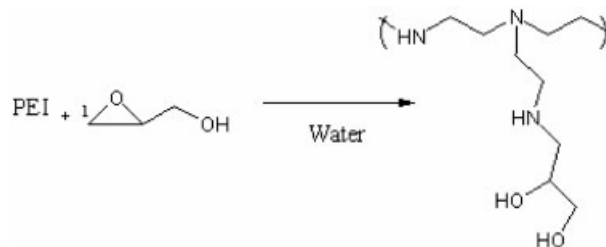


Figure 1 2,3-Dihydroxy propyl-PEI syntheses.

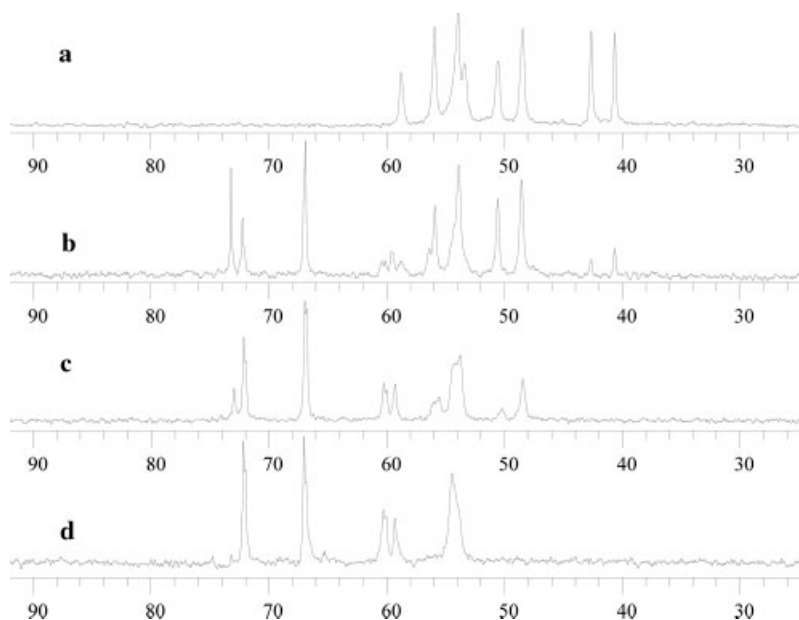


Figure 2 ^{13}C NMR spectra of (a) PEI, and its 2,3-dihydroxy propyl PEI polymers (b) 1/3, (c) 2/3, and (d) 3/3 functionalized.

based on our previous work where we determined that size-purified PEI has a $1^\circ : 2^\circ : 3^\circ$ amine ratio of approximately 1 : 1 : 1.⁴ These polymers were synthesized from commercially available glycidol by a trans epoxide ring-opening reaction with amine groups on the PEI backbone (Fig. 1). ^{13}C NMR was preferred to ^1H NMR for characterizing PEI and its derivatives, because of the large overlap of methylene signals in the ^1H spectrum. The ^{13}C NMR spectrum for PEI is shown in Figure 2, and exhibits characteristic signals for the CH_2 groups that have been assigned according to previous works.^{8–10} The ratio of primary (signals at 40.6 and 42.6 ppm), secondary (signals at 53.3, 50.5, and 48.4 ppm), and tertiary (signals at 58.5, 55.9, and 53.9 ppm) amino groups in the polymer backbone can be calculated from the signal integrals.⁴ Thus, NMR data indicate that the PEI sample consists of 35% primary amines, 34% secondary amines, and 31% tertiary amines.⁴ For the 2,3-dihydroxy propyl-PEI polymers, additional signals are detected and are associated with the presence of hydroxyl groups of the propyl diol substituents. For instance, the ^{13}C NMR spectrum for the 1/3-PEI shows one peak at about 67 ppm that is associated with CH_2 group nearest neighbors to OH groups, and a set of peaks from 72 to 73 ppm that is related with CH group nearest neighbors to OH groups.⁴ The same analysis applies for the other two PEI derivatives. Notice that all primary amines have reacted for the 2/3-PEI and that all primary and secondary amines have reacted for the 3/3-PEI. No reaction of glycidol was observed with the tertiary amines of PEI, in agreement with the considerably lower reactivity of these amines with glycidol for the model compound triethylamine.⁴ The degree of amine func-

tionization in the polymer backbone can be estimated by integrating the resonances in the ^{13}C spectrum. As a result, the estimated functionalization is about 30% for 1/3-PEI, 68% for the 2/3-PEI, and 100% for the 3/3-PEI, which is consistent with the ratio of added glycidol in the synthetic procedures.

High boron concentrations (above 1000 ppm)

A set of ^{11}B NMR experiments was initially performed to verify the boron concentration range where polyborate species do not occur in the presence of PEI. Figure 3 is an example of triborate and pentaborate structures, which are reported to exist at higher boron concentrations ($>0.25\text{M}$) and pH values ($>\text{pH } 6.5$).¹¹ We obtained ^{11}B NMR spectra for samples containing 1000–9000 ppm boron; both in the absence and presence of PEI. This polymer/polyelectrolyte was chosen because it does not form borate mono- or diester species, making it easier to detect additional peaks in the ^{11}B NMR spectrum. It is interesting to note that no polyborate species was observed in the absence of

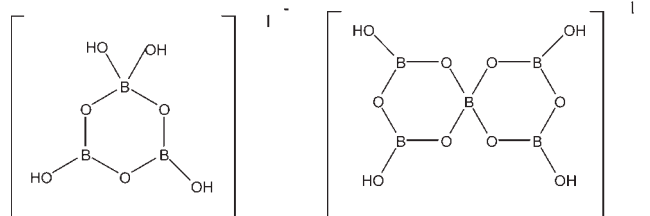


Figure 3 Triborate and pentaborate species that can occur under some conditions.

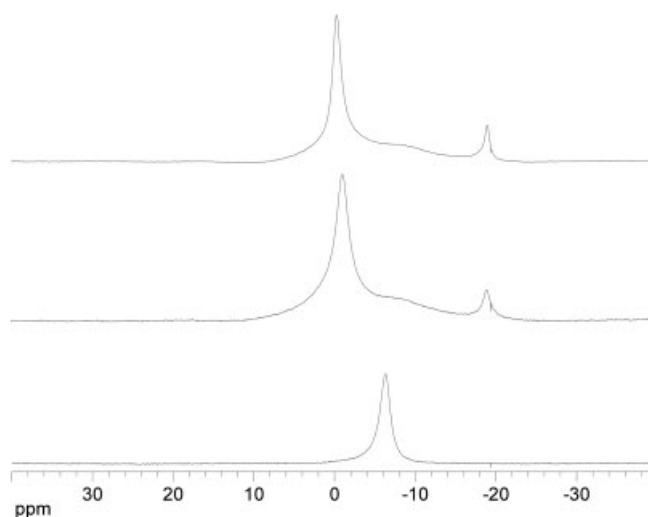


Figure 4 ^{11}B NMR spectra of 1% PEI in BA. From top to bottom: 9000 ppm B, 5000 ppm B, and 1000 ppm B.

PEI. For instance, ^{11}B spectra obtained for three boron concentrations at 9000, 5000, and 1000 ppm (pD values were 4.08, 4.95, 6.06; respectively) showed single peaks with chemical shifts at about 0 ppm. The reason for the lack of detection of polyborate species in these solutions was mainly due to low pD values.¹¹ BA solutions containing PEI showed the presence of polyborate species; additional peaks besides the one for BA were detected when 0.0775M PEI was added to 9000 ppm (pD was 6.06) and to 5000 ppm (pD was 7.14) BA solutions (see Fig. 4). Triborate species showed up as a broad single peak at -6.5 ppm due to rapid exchange between nonequivalent boron sites in this ion.¹¹ The narrower and upper field resonance at about -19 ppm was associated with pentaborate species.¹² No polyborate species was observed for 1000 ppm B in the presence of PEI (pD was 7.89). Only one peak was observed with a chemical shift of -6.5 ppm, which was associated with BA/borate species (see explanation below under ion-pairing section). This result indicates that boron concentrations below 1000 ppm should not give any interfering peaks in our ensuing ^{11}B NMR studies. The tetraborate dianion $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$

was not detected by ^{11}B NMR for any of the solutions investigated. The reasons probably being that (i) tetraborate does not exist to any extent in solution,¹¹ (ii) the signals for this ion are very broad, and (iii) signals are not observable by this technique due to NMR time-scale restrictions.⁹ This illustrates some of ^{11}B NMR limitations when applied to the detection of various polyborate species.

Low boron concentrations (below 1000 ppm)

To avoid the formation of polyborate species, the following experiments were performed with boron concentrations at and below 1000 ppm. In addition, boron concentrations of the order of 1000 ppm represent the upper-limit that occurs in primary coolant water of nuclear power plants. For these lower boron concentrations, BA can bind with the functionalized PEI through two distinct mechanisms: (i) borate ester formation through the attached ligand and (ii) ion-pairing formation with the backbone amines.⁴

Borate ester formation occurs either as a borate monoester and as borate diester as shown in Figure 5. ^{11}B NMR was employed to detect and quantify mono- and diester formation, since it is a powerful tool to study the structure of borate complexes.^{5,6} The complexation between BA/borate and 2,3-dihydroxy propyl sites is slow relative to the ^{11}B NMR time scale, consequently signals due to the ester complexes are observed separately from the BA/borate signal.⁶ ^{11}B NMR spectra were obtained at room temperature (22°C) for solutions of 2,3-dihydroxy propyl-PEI polymers containing boron concentrations ranging from 100 to 1000 ppm. We have detected three peaks in ^{11}B NMR spectra: BA/borate (variable chemical shift), monoester (-13.7 ppm), and diester (-9.8 ppm). For PEI, only one peak was detected and assigned to the BA/borate species. The ^{11}B NMR spectrum for the 1/3-PEI showed a higher concentration of borate monoester than borate diester. This result is reasonable since the amines in the 1/3-PEI are mainly mono-substituted (Fig. 6). Consequently, to form diester species boron must bind intramolecularly to another 2,3-dihydroxy

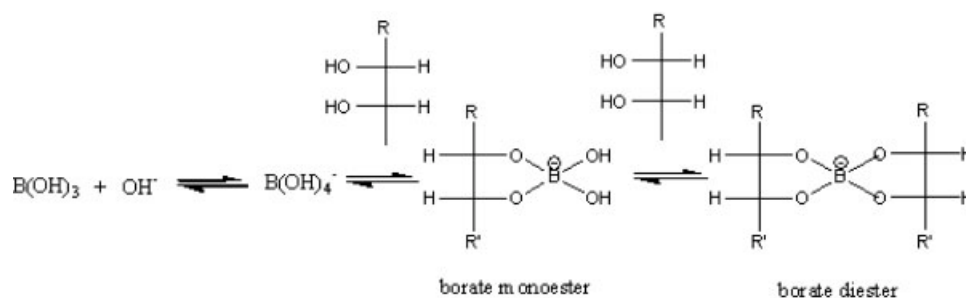


Figure 5 Binding of BA to two diol sites to form a stable tetradentate complex. R and R' can represent H or a carbon fragment or an attached polymer.

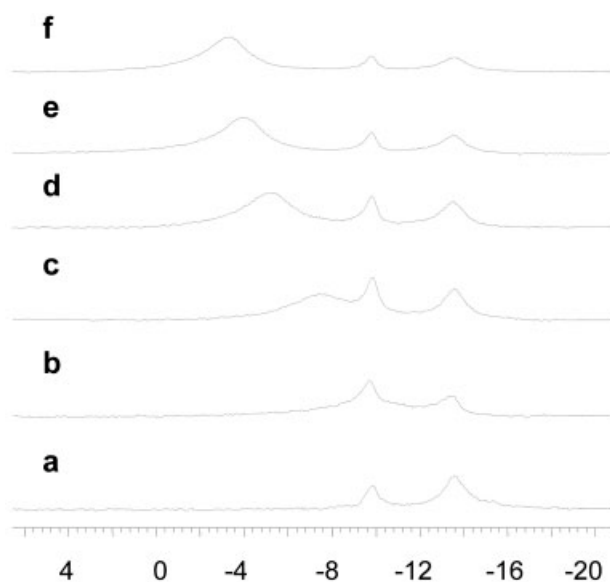


Figure 6 ^{11}B NMR spectrum for 1/3 functionalized PEI, in D_2O , and various BA concentrations: (a) 100 ppm, (b) 200 ppm, (c) 400 ppm, (d) 600 ppm, (e) 800 ppm, and (f) 1000 ppm.

propyl group on an adjacent branch, or intermolecularly between two macromolecules, or intramolecularly with small amount of disubstituted amine. Figure 7 shows ^{11}B NMR spectra for the 3/3-PEI, where the main ester peak is the one associated with diester species. This result indicates that diester formation has a higher binding constant than monoester formation. The same result was observed for the 2/3-PEI, i.e., a preference to form diesters over monoester species.

The boron binding capacity for each one of these three polymers was examined by plotting the combined relative abundance of mono and diester species

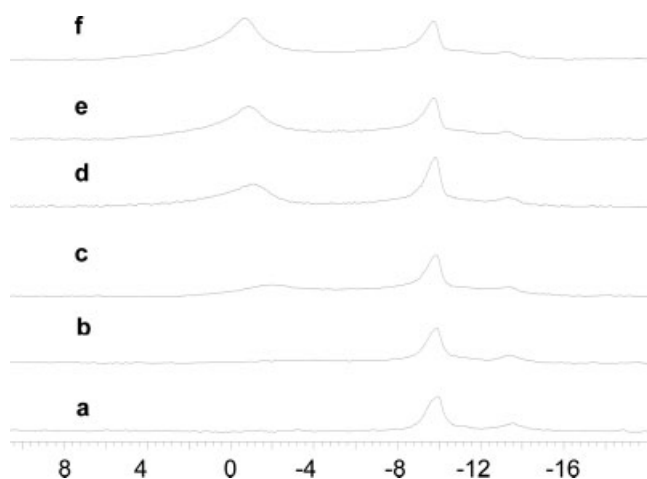


Figure 7 ^{11}B NMR spectrum for 3/3 functionalized 2,3-dihydroxy propyl-PEI, in D_2O , and various BA concentrations: (a) 100 ppm, (b) 200 ppm, (c) 400 ppm, (d) 600 ppm, (e) 800 ppm, and (f) 1000 ppm.

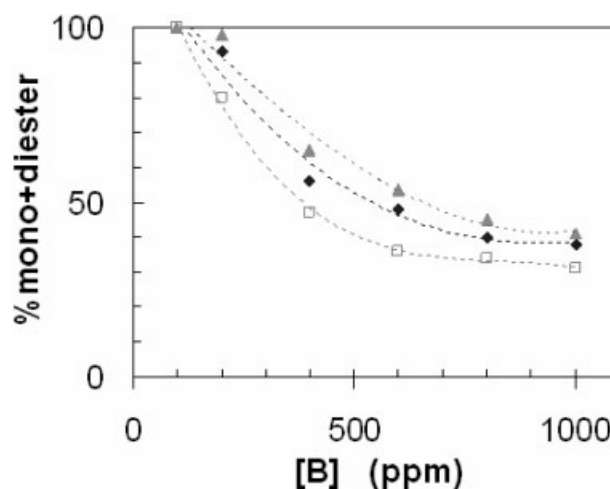
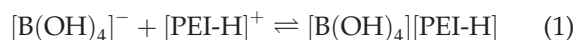


Figure 8 Combined percentage of monoester and diester for all three 2,3-dihydroxy propyl-PEI polymers as determined by ^{11}B NMR as a function of boron concentration. The BA concentrations varied from 1000 to 100 ppm: (\square) 1/3-PEI, (\blacktriangle) 2/3-PEI, and (\blacklozenge) 3/3-PEI.

as determined by ^{11}B NMR (Fig. 8). The 2/3-PEI performed better than the other two PEI derivatives on an equal molar basis, for any given boron concentration. The least functionalized 1/3-PEI showed the lowest monoester and diester content for any given boron concentration. It is interesting to notice that there is no unbound boron for 100 ppm concentration; all boron is bound to the polymer as a borate mono- or diester species for all three polymers. Table II lists K_d values obtained for the three PEI derivatives at 200 ppm B. It is readily evident that the 2/3-PEI has a much larger constant than the other two polymers under these binding conditions.

An ion-pairing mechanism can occur between borate anion and weak base anion exchange sites on the soluble polymer backbone as represented in eq. (1).



Thus, eq. (1) indicates that the pD value is an important parameter for determining the abundance of borate ions available for binding, as well as for establishing the degree of polymer protonation. For instance, high pD values lead to high borate content but low polymer protonation. Consequently, the greatest amount of ion-pairing occurs as a balance between high borate abun-

TABLE II
Calculated Formation Constants for 0.0775M
2,3-Dihydroxy Propyl PEI Polymers at 200 ppm B

Polymer	Borate ester (%)	pD	k_d
1/3-PEI	80	8.67	52
2/3-PEI	98	8.55	631
3/3-PEI	93	7.99	172

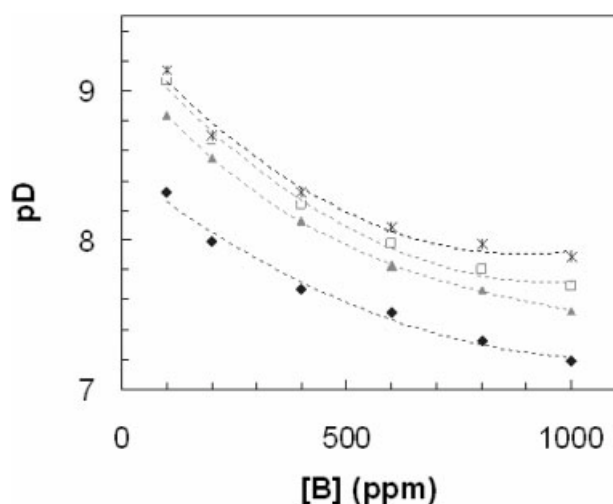


Figure 9 pD values obtained for PEI and its 2,3-dihydroxy propyl-PEI polymers as a function of boron concentration: (*) PEI, (□) 1/3-PEI, (▲) 2/3-PEI, and (◆) 3/3-PEI.

dance and high abundance of protonation sites. Figure 9 shows the pD values for PEI and its derivatives as a function of boron concentration. Independent of boron concentration and on an equal molar basis, the more basic polymer is PEI, followed by the 1/3, the 2/3, and finally the 3/3-PEI, or in other words, the greater the number of hydroxyl groups attached to the polymer backbone, the lower the polymer solution pD, or lower the basicity of the amines on the polymer, which is consistent with the electron withdrawing nature of hydroxyl groups.

The abundance of borate anions in the presence of the 2,3-dihydroxy propyl-PEI polymers can be probed by investigating the chemical shift of the BA/borate peak. This resonance is a function of pD, when the chemical shift is -17.7 ppm borate ions exists solely in the solution.¹³ The relative borate fraction is estimated by the comparison of the chemical shift relative to 100% BA (chemical shift 0 ppm against a 0.1M BA standard). Figure 10 shows relative borate anion abundances based on chemical shifts versus pD values for the three PEI derivatives at various boron concentrations (as plotted in Fig. 9). The 1/3-PEI solution had the largest percentage of borate ion formation (except at 100 ppm B where all the B was bound as borate esters for all polymers), whereas the fully functionalized PEI solution had the least amount of borate ion formation. As it has been mentioned before, ion-pair formation occurs between borate anions and protonated amines in the polymer backbone. Consequently, the chemical shift of the BA/borate peak is a measure of borate abundance, but it is not a direct measure of ion-pair formation. In spite of this limitation, it still can be used to estimate an upper limit for ion-pairing capacity. To estimate if there are enough weak anion exchange sites present in the polymer

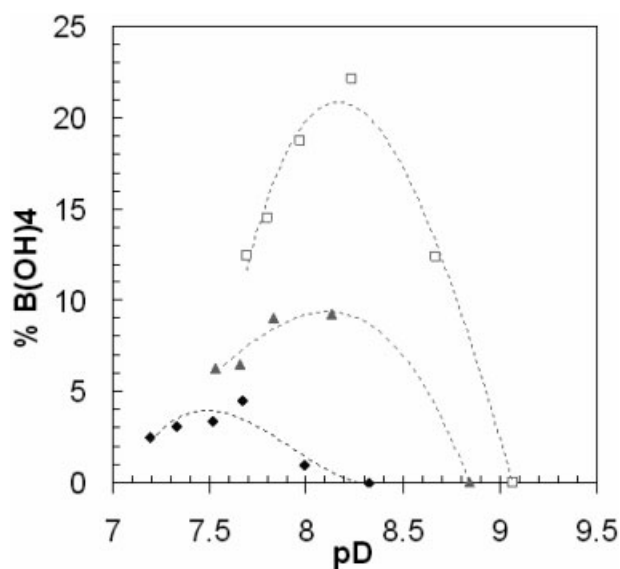


Figure 10 Percentage of borate for all three 2,3-dihydroxy propyl-PEI polymers as a function of pD. The BA concentrations varied from 1000 to 100 ppm: (□) 1/3-PEI, (▲) 2/3-PEI, and (◆) 3/3-PEI.

backbone to ion pair with the free borate, we can use previously reported titration data obtained for PEI.⁴ If 0.0775M PEI is present in solution, that represents at least one exchange site per average-repeat-unit (ARU) molecular weight (MW) or one in three of the amines is protonated at near neutral pH.⁴ The largest amount of free borate as estimated by NMR is 120 ppm at pH 7.7 for the 1/3-PEI solution. This boron concentration corresponds to ~ 7 times less borate anions than protonated sites for PEI. Consequently, there should be sufficient protonated sites in the polymer backbone to bind all the borate species. Table III lists the total amount of borate esters and borate anions. By assuming that all borate anions can be ion-paired to the polymer backbone, these numbers correspond to the estimated amount of boron that can be removed by the polymer-assisted ultrafiltration method. Thus, the 2/3-PEI polymer shows the best performance for overall boron binding. The question arises as to why

TABLE III
Summary of Total Possible Boron Binding as Borate Esters and Ion-Pairs for 2,3-Dihydroxy Propyl PEI Polymers

[B] (ppm)	% Possible total bound boron for 1/3-PEI	% Possible total bound boron for 2/3-PEI	% Possible total bound boron for 3/3-PEI
100	100	100	100
200	92.4	98	93
400	69	74	60.5
600	54.5	62.5	51.5
800	48.5	51.5	43
1000	42.5	47.5	40.5

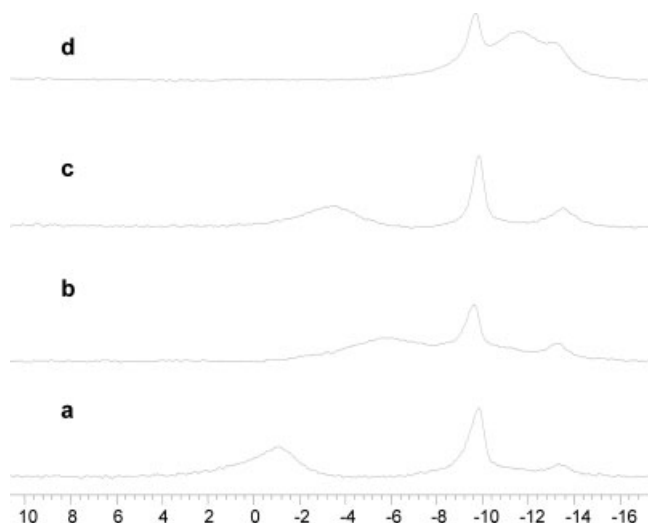


Figure 11 ^{11}B NMR spectra for (a) 3/3 diol 600 ppm B, (b) 3/3 diol 600 ppm B and 1M NaCl, (c) 2/3 diol 600 ppm B, (d) 2/3 diol 600 ppm B and 1M NaCl.

the 2/3-PEI binds better than the 3/3-PEI when the fully-functionalized polymer has more overall binding sites on a molar basis than the 2/3 functionalized polymer. We surmise that the answer is a balance between pD values and number of binding sites. The fully functionalized polymer has the most number of diol sites, many of them preorganized to give high-binding borate diesters. But as shown in Figure 9, this is the least basic of all three polymers with pD values mostly below 8. The 2/3-PEI has less binding sites, but its pD values vary between 8 and 9, a favorable range for borate ester formation.⁴

Salt studies

In a previous work,⁴ we made use of separation techniques (ICP-AES) to estimate the amount of bound boron for similar polymers as the ones investigated here. However, ICP-AES does not differentiate between the various boron binding mechanisms. Thus, to assess ester formation, we added NaCl to polymer/BA solutions to quench the ion-pairing mechanism. However, it was not known if salt addition could have some unanticipated effect on borate ester formation, which could bias the borate ester/borate ion-pairing ratio estimate. Thus, we examined by ^{11}B NMR the influence of adding a neutral D_2O solution of salt (NaCl) to the 2/3- and the 3/3-PEI polymers in the presence of BA. Solutions containing 1M in NaCl and 600 ppm boron were analyzed by and compared with their counterpart ones without NaCl. Surprisingly, the addition of nearly neutral NaCl resulted in very large increase in pD values, and as a consequence, an increase in chemical shifts of the BA/borate peak (Fig. 11). For instance, the pD for the 2/3-PEI changed from 7.83 to

9.54 when salt was added to the solution. The same effect was observed for the fully functionalized PEI, where pD changed from 7.52 to 9.02. A similar pD increase was also observed when 1M NaCl was added to 0.0775M PEI. A possible reason for the salt effect on pD values could be the displacement of hydroxyl groups from the cationic sites on the polymer backbone by chloride. This would release hydroxyl groups into the solution and thus increase pD. Another explanation for the pD increase could be a shift in the BA/borate equilibrium due to a displacement of borate anions from the ion pair by chloride. At this point, we have no clear evidence to support either conjecture. Furthermore, monoester and diester concentrations showed a decrease with salt addition. It changed from 53.5% to about 44% for the 2/3-PEI, and from 48% to about 36% for the 3/3-PEI. Thus, it appears that higher salt concentrations and pD values have promoted more borate formation at the expense of monoester and diester formation.

^{11}B NMR findings showed that salt addition has a detrimental result on ester formation and thus salt-suppression extractive techniques do not allow for a correct estimate of borate ester formation.

Variable temperature studies

Easy and straightforward reversal of boron binding is a very important factor for recycling ^{10}B -enriched BA in the nuclear power industry. Temperature reversal of boron binding is more amenable to nuclear power applications than the more often reported acid or base stripping.^{14,15} The facility of 2,3-dihydroxy propyl-PEI polymers to perform as temperature-reversible boron chelators was investigated for the 2/3 functionalized PEI polymer. This sample was prepared with 1% w/v

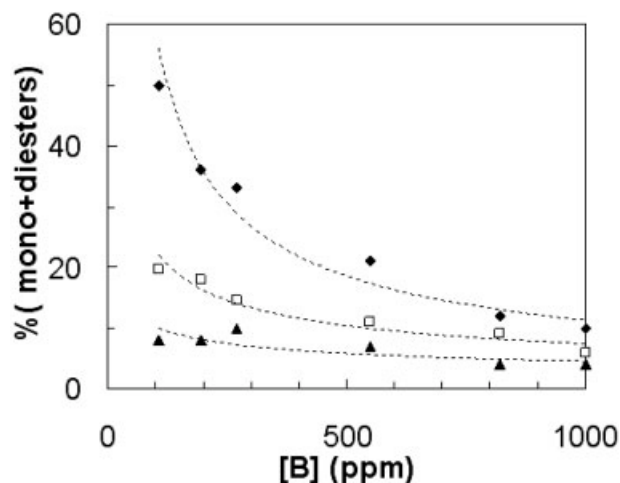


Figure 12 Relative abundance of mono- and diester for 2/3-PEI versus boron concentration at various temperatures: (◆) 25°C, (□) 45°C, and (▲) 65°C.

polymer concentration and for boron concentrations ranging from 1000 to 100 ppm. ^{11}B NMR spectra obtained from 25 to 65°C are shown in Figure 12. These results indicate that an increase in temperature to 65°C suppresses most borate ester formation for all boron concentrations. The binding capacity of these polymers is also reversible, i.e., it remains unchanged after various temperature cycles. In addition, binding of borates with anion exchange resins through ion-pairing has been reported to decrease as temperature rises.¹⁶ Consequently, the water-soluble polymers proposed in this study for BA recovery are expected to perform efficiently with regard to reversible boron binding as well.

CONCLUSIONS

We have synthesized and characterized new water-soluble PEI derivatives containing three levels of 2,3-dihydroxy propyl-ligands: 1/3, 2/3, and 3/3. These polymers were synthesized by functionalizing amino groups on the polymer backbone, and by attaching hydroxyl functional-groups through an oxirane ring-opening reaction. These PEI derivatives were especially designed to be used for boron removal and recycle in polymer-assisted ultrafiltration technology. We made use of ^{11}B NMR spectroscopy to evaluate boron-binding capacity and to identify boron-binding mechanisms. We found that the 1/3-PEI polymer favors the formation of borate monoesters over borate diesters. In contrast, borate diester formation predominated for the other two higher functionalized polymers. Overall, the 2/3-PEI polymer showed a better boron-binding capacity than the other two PEI derivatives for the sum of borate esters and ion-paired species. Estimates of the concentration of weak anion exchange sites available on the polymeric backbone indicated that there should be sufficient sites to bind all the borate ions available. The key to 2/3-PEI per-

formance is both a combination of polymer basicity and overall number and characteristic of diol binding sites. By employing ^{11}B NMR variable temperature, we have shown that ester concentration decreases dramatically at high temperatures. This is an important feature for considering the application of these water-soluble polymers in the nuclear power industry.

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