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Synthesis of polyaminostyrene-based and polyallylamine-based sorbents for boron removal

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ABSTRACT: Hydroxyalkyl derivatives of polyaminostyrene (PAS), polyallylamine (PAA), and polyethyleneimine (PEI) containing a 2,3-dihydroxypropyl moiety with a high degree of modification were synthesized. The chemical structures of the polymer transformation products were characterized with elemental analysis, Fourier transform infrared spectroscopy, ^{1}H-NMR spectroscopy, and ^{13}C-NMR spectroscopy in the solid state. PAS reacted with glycidol and formed poly[*N*-(2,3-dihydroxypropyl)aminostyrene] with a high degree of functionalization. PAA revealed primarily the graft polymerization of glycidol. In the case of PEI, primary amino groups allowed the formation of an *N*-derivative of 3-aminopropanediol-1,2. The PAA-based sorbent showed a high sorption capacity toward boron ions in both acidic and alkaline media. From the sorption isotherm data, the maximum sorption capacity of this sorbent at pH 4 was determined to be 3 mmol/g. The PAS-based resin maintained a high capacity between pH 9 and 12; the optimum pH was 12. The sorption capacity was 1.7 mmol/g. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43939.

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INTRODUCTION

The functionalization of polymers dramatically extends the ranges of the practically essential properties of known and commercial available polymer materials and, therefore, the fields of their application. The formation of new functional groups in the polymer structure greatly changes its properties and serves as a basis for its modern applications.[1–4] For instance, the introduction of the residues of polyol compounds into the polymer matrix allows one to obtain boron-specific sorbents because the vicinal diol functions help form chelates of four-coordinate boron.[5] The sorbents of boron known today, especially commercial ones, are formed on polystyrene,[6–14] polyallylamine (PAA),[15] polyethyleneimine (PEI),[16,17] chitosan,[18–22] and polymetacrylic acid[23–28] as a polymer matrix. Such a wide range of polymers is essential for the preconcentration and determination of boron with atomic absorption spectrometry and other spectroscopic techniques,[18,19] the recovery of boron from leaching and other technological solutions to semimetal resource utilization,[20–22,28] and the decontamination of natural and wastewaters from boron compounds.[9,11–14]

It is worth mentioning that the efficacy of the adsorption capacity to a great extent depends not only on the type of pendant functional groups but also on the nature, structure, crosslinking degree, and crystallinity of the polymeric matrix. Thus, for the formation of new highly effective sorbents, it is not only the nature of polymer backbone that is important but also the methods for its preparation and further functionalization. Despite the wide range of available sorbents of boron,[6–8,18,24–26] further development in this direction is impossible without a deeper understanding of the structure–property correlation and systematic studies of the effect of functional fragment structure and degree of substitution on the sorption characteristics. Furthermore, even though the high boron-binding ability of polyol compounds or saccharides is known, little attention has been paid to the influence of the polymer backbone structure on the boron sorption properties.

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To obtain a sorbent with a maximum sorption capacity, functionalization that leads to only a minimal increase in the molecular weight of the polymer unit is essential. A pendant group with a minimal molecular weight, containing vicinal hydroxyl groups, is the *N*-derivative of 3-aminopropanediol-1,2, formed during the reaction of amines with glycidol. In this article, we report on the synthesis of *N*-2,3-dihydroxypropyl derivatives of polyaminostyrene (PAS), PAA, and PEI and describe the effect of the polymer backbone structure on the boron sorption properties of these synthesized derivatives in comparison with known boron-specific sorbents.

EXPERIMENTAL

Materials and Methods

Linear polystyrene (molecular mass (MM) = 4×10^5 Da), crosslinked polystyrene (2% divinylbenzene), PAA hydrochloride, and branched PEI were purchased from Alfa Aesar. Glycidol (99.0%, Sigma-Aldrich) was used without purification. Tin(II) chloride dihydrate was recrystallized from water. All other chemicals were analytical grade and were used without further purification. PAS was treated ultrasonically with a homogenizer (SONOPULS HD 3200) with an operating frequency of 20 kHz. The degrees of nitration, reduction, and hydroxyalkylation were calculated from the elemental analysis data, determined by a PerkinElmer elemental analyzer.

The degree of hydroxyalkylation was calculated from the element analysis data as follows:

$$\text{Degree of hydroxyalkylation} = [(\text{C/N})_p - (\text{C/N})_{ip}]/3$$

where C/N is the molar ratio of the elements in the product (*p*) and the initial polymer (*ip*) and 3 is the number of carbon atoms in glycidol.

The degree of functionalization by vicinal diol groups was measured with well-known methods.[29] Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer Spectrum One FTIR spectrometer with a diffuse reflectance sampling accessory.

Solid-state ^{13}C-NMR spectra (126 MHz) were recorded with methods of cross-polarization with rotation at the magic angle (cross-polarization/magic angle spinning) on a Bruker Avance-500 spectrometer with a rotor diameter of 4 mm and a rotation frequency of 5000 Hz. High-resolution ^{1}H-NMR spectra were recorded on the Bruker Avance-500 spectrometer at 70 °C to increase the solubility of the samples and to obtain better spectral resolution. The samples were dissolved in deuterium oxide/deuterium chloride (concentration = 10 mg/mL), and sodium 3-(trimethylsilyl)-1-propanesulfonate was used as an internal standard. The suppression of the solvent signal during the spectrum recording was realized with the presaturation technique.

Preparation of Polystyrene Derivatives

Nitration and the further reduction of polystyrene were performed, as described in a previous article.[13] The treatment of crosslinked PAS with glycidol was performed under the following conditions.[13]

Method 1. The PAS (2.0 g/0.016 mol of NH_2 groups) and 50 mL of water were mixed mechanically until the suspension formed. Then, 1.0 mL (0.016 mol) of glycidol was added, and the mixture was treated ultrasonically for 40 min. After cooling, 50 mL of distilled water were added to the ending mixture. The product was precipitated with acetone, extracted by hot ethanol (EtOH) for 24 h, and dried at 50 °C to a constant weight.

Method 2. The mixture of 2.0 g (0.016 mol of NH_2 groups) of PAS and 2 mL of concentrated HCl was kept about 10 min until the formation of the gel-like mass. Then, 1.0 mL (0.016 mol) of glycidol was added; the mixture was heated at 60 °C for 18 h and then cooled. To the mixture, 5 mL of distilled water was added; then, after homogenization, the product was precipitated with acetone, extracted by hot EtOH for 24 h, and dried at 50 °C to a constant weight.

The conditions for PAS modifications with glycidol and the characteristics of the products are given in Table I.

Preparation of the PAA and PEI Derivatives

PAA hydrochloride was transferred into the base state by sodium hydroxide with further precipitation of the polymer from the aqueous solution with acetone and drying at room temperature. Glycidol treatment was performed under homogeneous reaction conditions with a similar scheme: the mixture of 2.35 g (0.05 mol of NH_2 groups) of PAA, 25 mL of water, and 19.5 mL (0.3 mol) of glycidol was heated up to 60 °C for 14 h and cooled. The product was reprecipitated with acetone twice and then dried at ambient temperature to a constant weight. PEI was functionalized in the same manner but with a mixture of 2.2 g (0.051 mol of NH_2 groups) of PEI, 25 mL of water and 14.8 mL (0.2 mol) of glycidol. The conditions for modification of PAA and PEI with glycidol and the characteristics of the product are shown in Table I.

To obtain insoluble sorbents, 0.1 mol of hydroxypropylated PAA or PEI was mixed with 250 mL of water containing 0.4 g of NaOH, and 0.78 mL of epichlorohydrine was added to the mixture under constant stirring. After the mixture was heated at 50 °C for 2 h, the precipitate was filtered, washed with water until there was a negative reaction to Cl^- ions, and dried at 50 °C to a constant weight.

Sorption Experiments

Sorption experiments were carried out at a temperature of 25 °C. To study the sorption properties, 0.1 g of sorbent (particle size = 50 μm) was shaken in plastic flasks with a 5-mL solution containing boron ions for 24–72 h at 200 rpm. The initial concentrations of boron were from 0.05 to 0.88 mol/dm. The pH value of the boron solution was adjusted with hydrochloric acid and sodium hydroxide to prevent the effect of buffers. The sorption capacities were calculated with the difference in the initial concentration and equilibrium concentration of the boron ions determined by inductively coupled plasma atomic emission spectroscopy with a PerkinElmer Optima 4300 DV spectrometer. The low concentration of boron ions in the solution was measured with titrimetric analysis.[29] The ion-exchange isotherms of boron ions were obtained at 25 °C for poly[*N*-(2,3-dihydroxypropyl)allylamine] (PHAA) with a degree of substitution of 2.9 at pH 4 and 12 and for poly[*N*-(2,3-

Table I. Conditions of the Hydroxyalkylation of Polyamines with Glycidol and Characteristics of the Obtained Products

Polymer	Reaction conditions		Degree of hydroxyalkylation
	Molar ratio of NH_2 to glycidol	Polymer concentration (%)	
PAS $[C_8H_{6.6}(NO_2)_{0.4}(NH_2)_{1.0}]$	1/3[a]	4 (dispersion)	2.1
	1/3[b]	4 (dispersion)	1.4
	1/5[a]	6 (dispersion)	2.2
Crosslinked (2%) PAS $[C_8H_{6.5}(NO_2)_{0.8}(NH_2)_{0.7}]$	1/6[a]	23 (dispersion)	2.1
	1/6[b]	23 (dispersion)	3.3
PAA[b]	1/2	8	1.8
	1/4	8	3.0
	1/5	8	3.4
	1/6	8	3.3
PEI[b]	1/1	15	0.9
	1/2	15	1.5
	1/3	15	1.9
	1/4	15	2.1

[a] The reactions were performed with an ultrasonic treatment for 40 min (method 1).
[b] The reactions were performed under heating (60 °C) for 12 h (method 2).

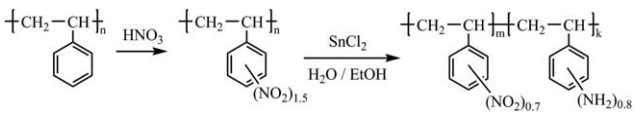
dihydroxypropyl)aminostyrene] (PHAS) with a degree of substitution of 2.3 at pH 12.[30,31]

RESULTS AND DISCUSSION

Modification of PAS

The modification of PAA, PEI, and presynthesized PAS crosslinked with divinylbenzene (2%) by glycidol were performed under the conditions of polymer transformations investigated earlier.[13,21,22] The crosslinked PAS was used to minimize the swelling of the ending product and was synthesized through the sequential nitration and reduction of crosslinked polystyrene by methods already known (Scheme 1).

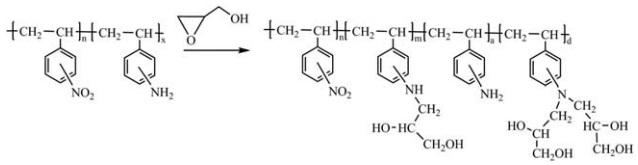
As shown in the data in Table I, the reactivity of the crosslinked and noncrosslinked polystyrene in the nitration process was the same, but in the reduction reaction, the presence of crosslinking significantly reduced the reactivity of the polymer because the degree of reduction did not exceed 50% in comparison with the 70–80% reduction in the case of the noncrosslinked polystyrene.[13] Crosslinking had the same effect on the reaction of PAS with glycidol (Scheme 2). The maximum degree of hydroxyalkylation for the crosslinked polymer was achieved with a higher molar excess of glycidol and a higher dispersion as compared to those in noncrosslinked PAS (Table I). The composition and structure of the derivatives were characterized with the data of elemental analysis and FTIR spectroscopy [Figures 1(S)–3(S) in the Supporting Information].



Scheme 1. Sequential nitration and reduction of crosslinked polystyrene.

The analysis of the FTIR spectra of PHAS demonstrated that aside from the absorption band characteristic for the PAS molecule at 3339 (N—H), 2916 and 2881 (C—H), 1616 (C═C), and 1512 (N—O) cm^{-1}, there emerged new bands at 3346 (O—H) and 1038 (C—N) cm^{-1}; these indicated the successful functionalization of the amino group by dihydroxypropyl radicals. To determine more unambiguously the chemical structure of PHAS, we used solid-state ^{13}C-NMR spectroscopy. In the spectrum of the product (Figure 1), there were signals of carbon atoms of polystyrene backbone with chemical shifts at 34 ppm (C1), 39 ppm (C2), 106 ppm (C5), 126 ppm (C3, C4), and 146 ppm (C6) [32] and signals of carbon atoms of *N*-substituted 3-aminopropanediol-1,2 with chemical shifts at 54 ppm (C7), 63 ppm (C8), and 70 ppm (C9).[24,33] The presence of other signals was caused by the probable partial oxidation of amino groups with the formation of a quinone structure [signal at 185 ppm (C10)]; this could further react with the amino group to form imine [signal at 167 ppm (C11)] and with the hydroxyl group to form a hemiacetal group [signal at 86 ppm (C12)]. The formation of the two latter functional groups created additional crosslinking for PHAS.

As shown in the FTIR and ^{13}C-NMR data, glycidol reacted with the amino groups. It is known that glycidol reacts with amines by Krasuski's rule,[34] whereas in the presence of an acid catalyst, a mixture of two isomers is formed.[35] Indeed, as followed from



Scheme 2. Preparation of the crosslinked (2% divinylbenzene) PHAS.

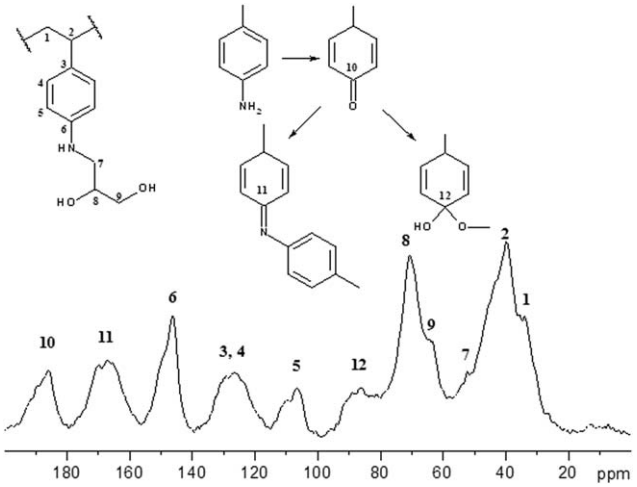


Figure 1. ^{13}C-NMR magic angle spinning spectrum (126 MHz) of crosslinked (2% divinylbenzene) PHAS.

the results of the determination of vicinal hydroxyl groups in the PHAS samples, which appeared as a result of opening the epoxide cycle by the rule, their quantity was 70% of the overall degree of hydroxyalkylation. The ^{13}C-NMR data also supported the preferable course of the reaction in accordance with the rule because there were three signals of carbon atoms of 2,3-dihydroxopropyl groups in the product spectrum but not two of them, as in *N*-substituted 2-aminopropanediol-1,3.

Comparative Reactivity of the Amino Polymers with Glycidol

The analysis of the polyamine backbone influence on the reaction with glycidol (Table I) showed that PAA had a much greater reactivity compared to PAS because of the greater nucleophilicity of the amino group presupposed by the aliphatic nature of PAA. In the case of PAS, the nucleophilicity of the amino group was greatly reduced under the influence of the aromatic ring, as happens in low-molecular amines.[36] An increase in the molar excess of glycidol toward the PAA amino groups led to a significant value growth in the degree of hydroxyalkylation, as the elemental analysis data showed (Table I), but a value over 2 indicated the graft polymerization of glycidol[37] on PAA (Scheme 3).

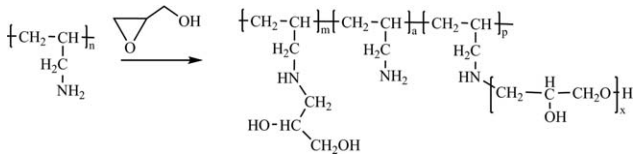
According to the FTIR spectroscopy data, the relative absorption band intensities increased at 3351 cm^{-1} (N—H, O—H), 2927 cm^{-1} (C—H), and 1040–1106 cm^{-1} (C—N,C—O) in comparison with the original PAA spectrum; this indicated the successful reaction of polymer transformation. As follows from the ^{1}H-NMR data (Figure S4 in the Supporting Information), in the spectrum of PHAA, the signals of hydrogen atoms of the PAA backbone at 1.44, 2.61, and 3.53 ppm and that of 1,3-disubstituted isopropyl alcohol within the interval 3.53–4.01 ppm were observed. Two signals of *N*-disubstituted 2-aminopropanediol-1,3 with any comparable integral intensity in the spectrum are not shown. Further determination of vicinal diol groups in the samples of PHAA, which appeared as a result of the opening of the epoxide cycle by Krasuski's rule, showed that their quantity did not exceed 10% of the overall degree of hydroxyalkylation. Therefore, a significant increase in the Lewis basicity with the transition from PAS to PAA led to the fact that during the reaction with glycidol, its polymerization increased significantly because of the catalytic action of amino groups. As a much weaker base, PAS did not promote this process; it only took part in the slower reaction of nucleophilic substitution.

In analogous conditions, PEI showed a reactivity similar to that of PAS (Table I), despite its aliphatic nature, as in the case with PAA. The reason was the branched structure of the polymer and the smaller quantity of amino groups in the polymer volume unit in comparison with PAA. Significant steric hindrance decreased the nucleophilicity of the primary amino groups. As a result, it became comparable with the basicity of the PAS amino groups; this decreased as a result of the electron influence of the aromatic ring. As the detailed study of the interaction of PEI and glycidol showed,[16] only 95% of the overall quantity of glycidol reacted with the primary amino groups; this was caused by the steric hindrance of amino groups. It is worth mentioning that PEI showed a higher reactivity compared with the data.[16] The same effect has been previously observed for chitosan[38] and PAA[39] as a gel-synthesis effect. Indeed, the transformation of PEI in the concentrated gel (15%) increased the degree of functionalization from 25 to 100% despite the minimal value of the reaction temperature.

Sorption Properties of PHAS and PHAA toward Boron Ions

Further crosslinking of the chelating PHAS-based sorbents was not performed because the product possessed a low degree of swelling in the aqueous solution. The PHAA-based sorbent was synthesized through crosslinking by epichlorhydrine, whereas poly(*N*-2,3-dihydroxy)propylethyleneimine under similar conditions could not be crosslinked, despite the multiple repetitions of the procedure; this may signify the fact that the preparation of the PEI-based sorbent required prior crosslinking of the polymer and only then could it be functionalized by hydrophile groups.[17]

The pH dependence of the sorption of boron ions (Figure 2) showed that in acidic media, the fixation of boric acid by PHAS and PHAA sorbents was provided by ion exchange. Earlier, through the example of PAS and PHAA, it was shown[13] that in such conditions, the presence of 2,3-dihydroxypropyl groups did not affect the sorption value; therefore, the PHAS polymer hydroxyl groups did not participate in the sorption. The PHAA-based sorbent in acidic media showed six times more sorption capacity than the PHAS sorbent. The increase in sorption capacity could be partially explained by the fact that the PHAA had a stronger base and a larger quantity of anion-exchange centers. However, to justify the six-fold growth, we have to maintain that in this case, along with ion exchange, the sorption



Scheme 3. Reaction of glycidol with PAA.

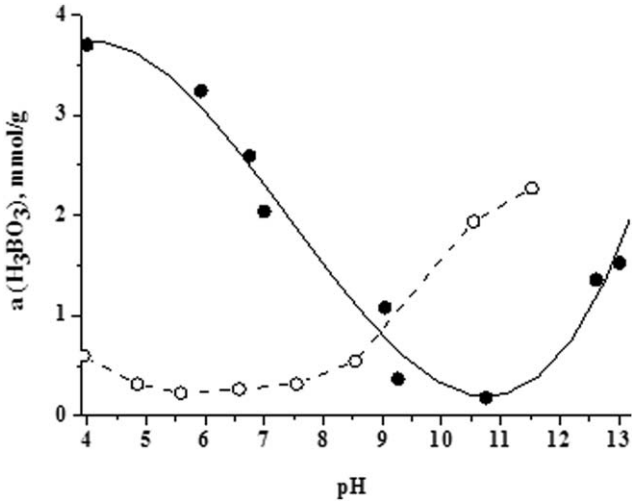


Figure 2. pH dependence of the sorption of boron by (○) PHAS (degree of hydroxyalkylation = 2.3) and (●) PHAA (degree of hydroxyalkylation = 3.3) with an initial concentration of boron of 0.78 mol/L at 25 °C. a(H_3BO_3) - Sorption capacity of H_3BO_3.

proceeded in the presence of the hydroxyl groups of the sorbent because of the formation of boric acid ethers.[16]

When the pH value increased, the sorption capacity of PHAS grew to a large extent, whereas PHAA did not provide such a fixation of boron ions. Taking into account the behavior of boron-containing ions in the aqueous solution[20,40] and the binding ability of hydroxyl groups with anion borate,[5,7,41,42] such a change in the sorption capacity became more understandable. When the pH value was increased, the quantity of anion-exchange centers significantly decreased, whereas the binding ability of the hydroxyl groups increased. This might possibly have been promoted either by the shift in the dissociation balance of the hydroxyl groups of amino hydroxyl fragments or by the transition of borate oligomer forms in alkaline media in monoborate ion $B(OH)_4^-$. The sorbents with amino hydroxyl functional groups behaved in a similar way with the change in pH.[15,25,43,44]

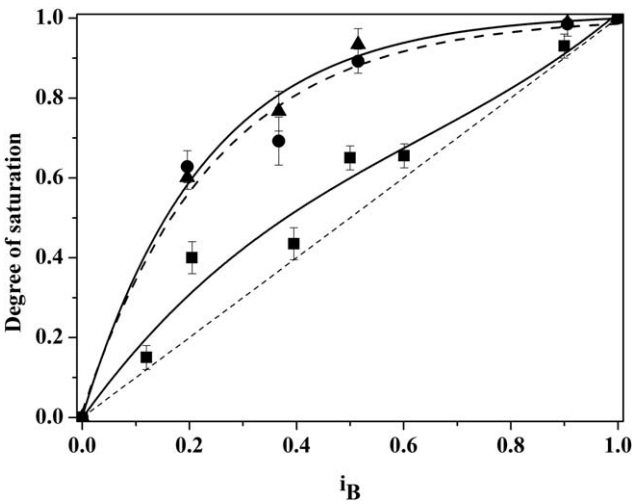


Figure 3. Ion-exchange isotherms of boron at 25 °C for (■) PHAA at pH 4 and (▲) PHAS and (●) PHAA at pH 12. The degree of saturation is the equivalent ionic fraction of boron in the sorbent. i_B = equivalent ionic fraction of boron in the solution

It is noteworthy that there was a difference in the sorption properties of PHAS and PHAA both in acidic and alkaline media (Figure 2). This difference obviously characterized the influence of the distance between the amino group and the hydroxyl groups on the boron ion sorption. To provide effective sorption in alkaline media, the presence of the residue of *N*-substituted 2-aminopropanediol was only necessitated, not a large amount of hydroxyl groups, which, by way of example, polyglycerol in PHAA provided.

The ion-exchange isotherms of boron ions by the PHAS and PHAA sorbents are shown in Figure 3. The growth of the boron concentration in solution led to an increase in its sorption capacity in alkaline media by both of the sorbents. In acidic media, a sharp increase in the sorption capacity was only observed for PHAA. For PHAS, the sorption capacity was minimal, and when the solution was diluted, it quickly fells to zero. A mathematical analysis of the experimental data showed that at pH 12, the maximum sorption capacity was 1.68 mmol/g for PHAS and 1.40 mmol/g for PHAA. At pH 4, this value for PHAA was 2.96 mmol/g.

As demonstrated earlier,[13] under such conditions, the sorption capacity of PHAS grew with increasing degree of substitution. Obviously, the sorption capacity for PHAA also grew with the increase in the degree of hydroxyalkylation. This explained the differences in the value of boron sorption shown in Figures 2 and 3.

The ion-exchange isotherms of boron at pH 12 for PHAS and PHAA (Figure 3) demonstrated the growth of sorption capacity with the sorbent saturation.[30,31] This form of isotherm was characteristic in case of the sorption of larger organic ions, which interacted very forcefully. The curve signified the realization of boron oligomerization on the surface of sorbents simultaneously with the binding process at such high concentrations of the equilibrium solution. The S-shape of the isotherm for PHAA at pH 4 was possibly related to the simultaneous realization of the two mechanisms of boron sorption. This agreed very well with the conclusions we made earlier during the analysis of the curves in Figure 2 about the coexistence of ion exchange and the formation of boric acid ethers with the hydroxyl groups of the sorbent.

CONCLUSIONS

A comparative analysis of reactivity for a number of polymers containing amino groups in their interaction with glycidol was performed. According to the analysis of the structure of the polymer products, we found that PAS prepared through the sequential nitration and reduction of crosslinked polystyrene reacted with glycidol to form PHAS with a maximum degree of functionalization. In the case of PAA, we mostly observed the graft polymerization of glycidol. The primary amino groups of PEI allowed formation of an *N*-derivative of 3-aminopropanediol-1,2. The difference in the structure of the established derivatives greatly influenced the sorption properties

toward boron. The sorption capacity of the synthesized polymers depended on the degree of substitution by vicinal diol groups. The PAA-based sorbent revealed high capacity values, either in acidic or alkaline media. The maximum sorption value at pH 4 for the PHAA sorbent with a degree of hydroxyalkylation of 2.9 was 3 mmol/g. The sorption capacity of PHAS dropped significantly with decreasing pH value; the maximum sorption of boron at pH 12 was 1.68 mmol/g.

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