

Functionalization of Polymer-Supported Pentaerythritol as a General Synthesis for the Preparation of Ion-Binding Polymers

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ABSTRACT: Pentaerythritol bonded to cross-linked poly(vinylbenzyl chloride) beads (PE) provides a scaffold onto which ligands can be attached by reaction with reactive compounds such as phosphoryl halides. To broaden the applicability of PE for the preparation of ion-selective polymers, conditions are reported for the conversion of the hydroxyl group to the bromide, which acts as a better leaving group. The $-\text{CH}_2\text{Br}$ moiety thus provides a handle on which an array of ligands can be bound through nucleophilic substitution. In this first in a series of reports, immobilization of diethylamine onto the PE and the ion-binding affinities of the resulting polymer are described. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Functionalized pentaerythritol has numerous applications in separations,¹ as flame retardants,² surfactants,³ antioxidants,⁴ crosslinking agents,⁵ polyoxometalate derivatives,⁶ and metal-containing catalysts.⁷ The hydroxyl groups are functionalized by reaction with reactive groups such as acyl chlorides⁸ or anhydrides.⁹ However, for reactions requiring nucleophilic substitution at the methylene carbon, functionalization must be preceded by conversion of the $-\text{OH}$ into a better leaving group.¹⁰

Immobilizing pentaerythritol onto cross-linked poly(vinylbenzyl chloride) has led to the preparation of a new polymer-supported reagent for metal ion separations after monofunctionalization by a phosphoryl chloride to give a neutral phosphate diester ligand that becomes the site of metal ion binding: the two remaining $-\text{CH}_2\text{OH}$ groups act as auxiliary groups to increase the binding ability of the phosphate by affecting the electron density at the phosphoryl oxygen through hydrogen bonding.¹¹ To broaden the applicability of immobilized pentaerythritol to the preparation of a variety of ion-binding polymers, it was necessary to develop a general method for converting the $-\text{OH}$ into a better leaving group. Because the $-\text{CH}_2\text{Br}$ moiety is prone to nucleophilic attack and the conversion of soluble pentaerythritol to the bromide with PBr_3 is well known,¹² this approach was taken here. The utility of the resulting polymer was then explored by its conversion to the ion-binding amine ligand, given especially that aminated polymers are applied to

environmental remediation,¹³ wastewater treatment,¹⁴ chromatographic separations,¹⁵ and catalysis.¹⁶

EXPERIMENTAL

Materials

The copolymer of vinylbenzyl chloride (VBC) and 2 wt % divinylbenzene (DVB) was prepared by suspension polymerization with 0.5 wt % benzoyl peroxide as initiator. After polymerization, the beads were extracted with toluene, dried, and sieved to recover a particle size of 425–600 μm . VBC, DVB, pentaerythritol, phosphorus tribromide, diethylamine, organic solvents, metal nitrate salts, and metal standard solutions were purchased from Fisher Scientific or Sigma–Aldrich and used directly without further treatment.

Synthesis of Immobilized Pentaerythritol (PE)

Eight grams of NaH (60% dispersion) was slowly added to 60.0 g of pentaerythritol in 200 mL of *N*-methylpyrrolidone (NMP) in a 500 mL round-bottom flask fitted with a condenser, overhead stirrer, and gas inlet tube. The mixture was stirred at room temperature under N_2 flow for 2 h. To the resulting solution, 6.0 g of polyVBC beads swollen in 40 mL NMP for 2 h was added. The mixture was kept at 80°C for 20 h. The solution was removed, the beads were washed with NMP, NMP/water (1 : 1) and water, and vacuum-dried at 70°C for 12 h.

Bromination of PE (PE-Br)

Two grams of PE were swollen in 100 mL of 1,2-dichloroethane in a 250 mL round-bottom flask fitted with an

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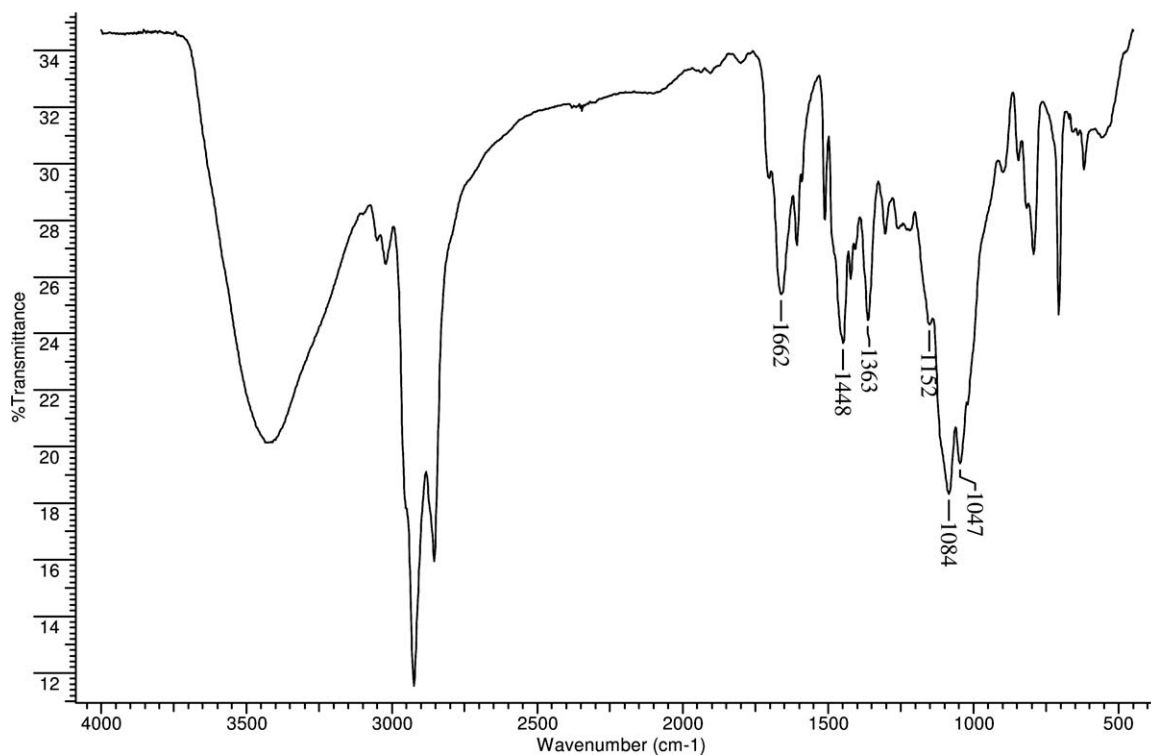


Figure 1. FTIR spectrum of polyVBC-bound pentaerythritol (PE).

overhead stirrer for 20 min and then 0.10–2.50 mL PBr_3 added. The mixture was stirred at 23°C for 168 h. The solution was removed and the beads were washed with 1,2-

dichloroethane, acetone, and water, then vacuum-oven dried at 70°C. The bromine capacities were determined by Galbraith Laboratories (Knoxville, TN).

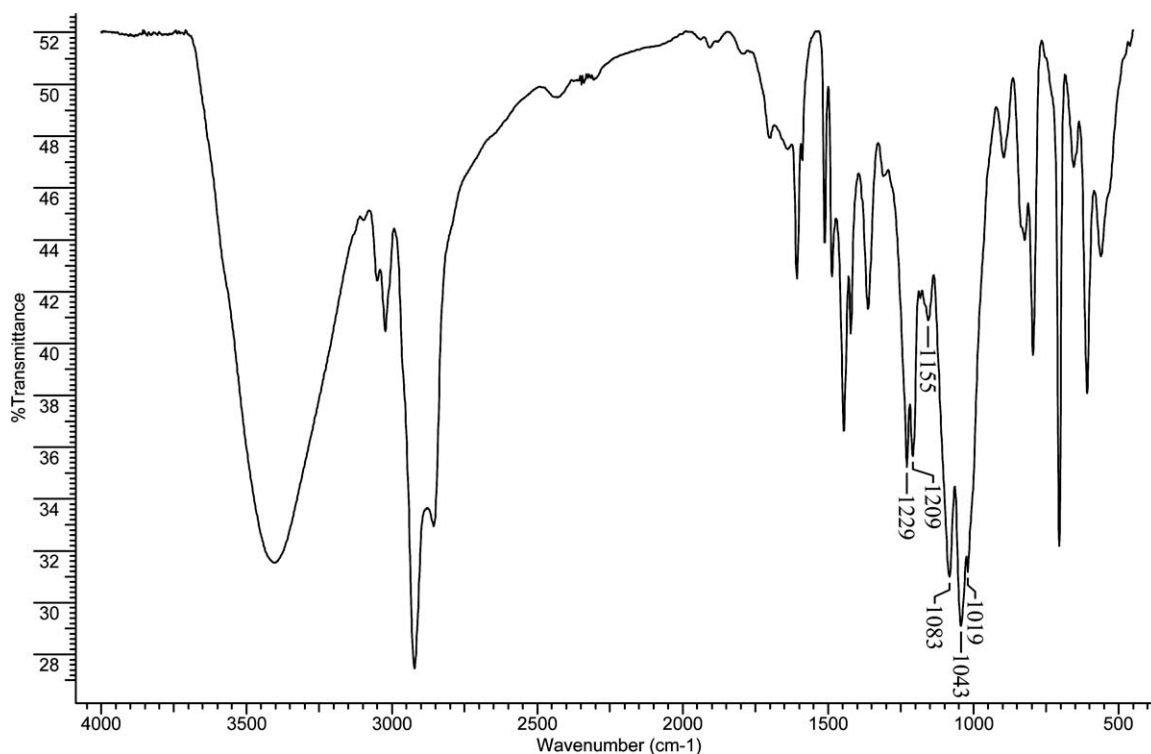


Figure 2. FTIR spectrum of polyVBC-bound brominated pentaerythritol (PE-Br): 0.20 mL PBr_3 .

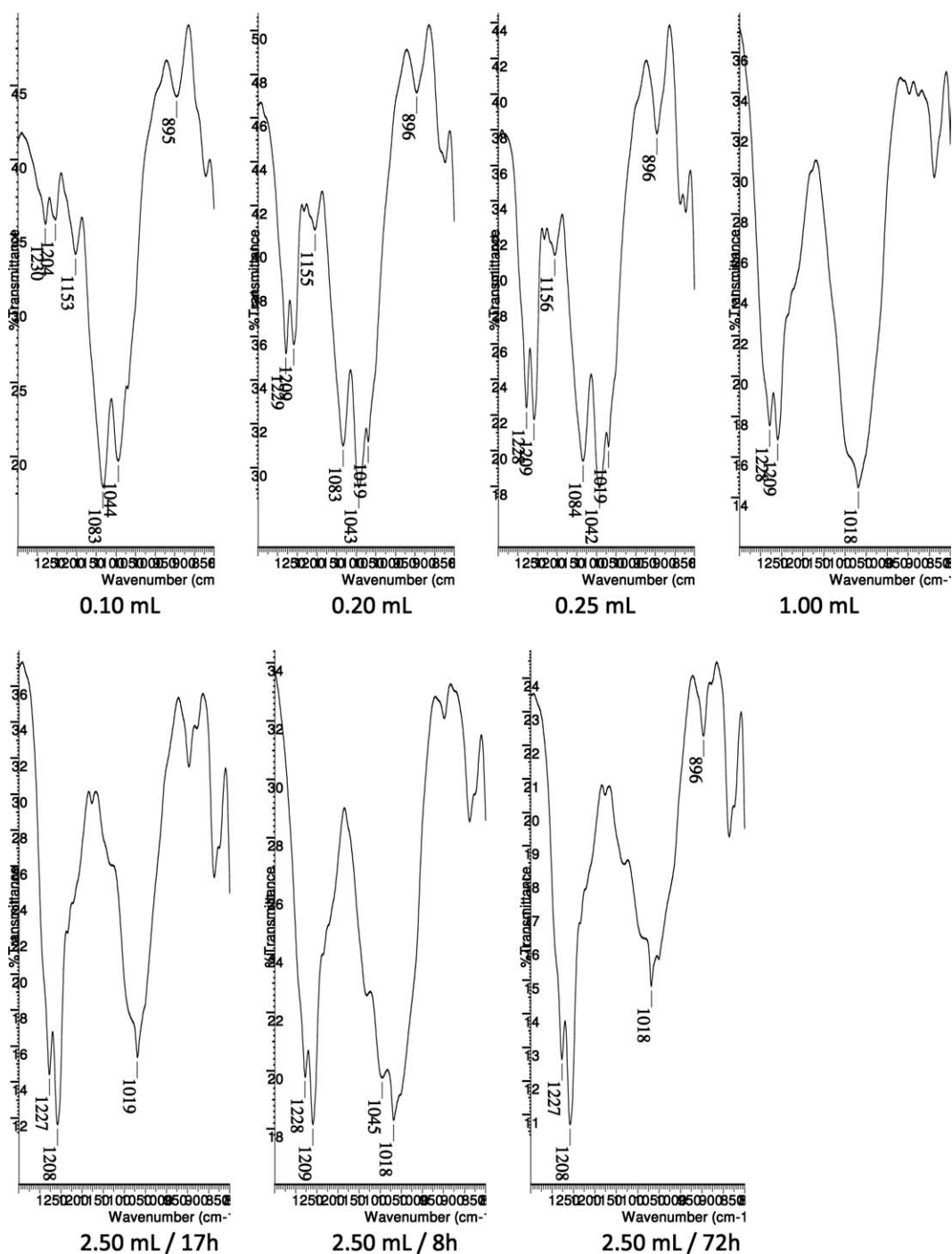


Figure 3. FTIR spectra in the region $800\text{--}1300\text{ cm}^{-1}$ for polymers prepared from PE and varying amounts of PBr₃ (unless otherwise indicated, the reaction time is 17 h).

Amination of PE-Br (PE-N)

Two grams of PE-Br was mixed with 20 mL diethylamine in 100 mL of NMP in a 250 mL round-bottom flask fitted with a condenser, thermometer, and overhead stirrer. The mixture was stirred at 60°C for 17 h. The beads were washed with NMP, NMP/water (1 : 1) and water, then conditioned with 1 L each of 1.0 N NaOH, water, 1.0 N HCl and water to ensure complete conversion to the protonated form.

Synthesis of Immobilized Diethylamine (NEt_2)

PolyVBC beads (5.0 g) were heated at 60°C with 10 mL of NMP and 40 mL of diethylamine for 17 h. The solution was removed and the beads were washed with NMP and water, then conditioned as above.

Characterization

Spectra were obtained with a Perkin–Elmer Spectrum 65 Fourier transform infrared spectrometer. Sixteen scans with a resolution

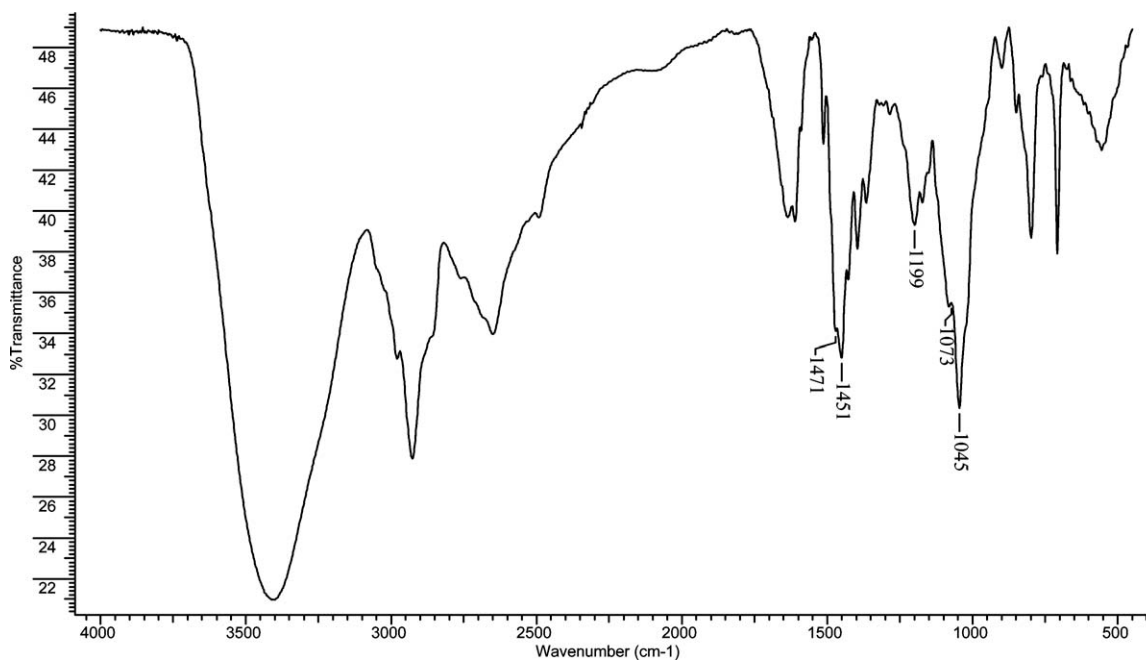


Figure 4. FTIR spectrum of PE-Br aminated with diethylamine (PE-N).

of 4 cm^{-1} was averaged for each spectrum. The phosphorus capacity was measured after mineralization of 20 mg of resin in concentrated sulfuric acid in the presence of copper sulfate and subsequent reaction with ammonium vanadate-molybdate. The intensity of yellow coloration was measured at 470 nm on a Spectronic 21D (Milton Roy). The nitrogen capacity was determined by the Kjeldahl method after oxidation of 200 mg of polymer in 25 mL of concentrated sulfuric acid containing 250 mg of copper sulfate and 10 g of potassium sulfate. The chlorine capacity was determined by combusting 100 mg of polymer in an oxygen-filled bomb and titrating the resulting solution with potassium thiocyanate.

Metal Ion Affinity Study

The metal ion affinities were determined by batch equilibration using 10^{-4} N metal ion solutions (except for uranyl which was 10^{-4} M) in 0.01–1.0 N nitric or sulfuric acid. Enough Buchner-dried resin to give 0.50 mmol nitrogen was shaken with 5.0 mL of metal ion solution for 17 h after it was pre-equilibrated three times with the appropriate background solution (each shaken for 15 min). The metal ions include Pb(II), Cu(II), Cd(II), Zn(II), La(III), Lu(III), Al(III), and U(VI). All were prepared from their nitrate salts except uranium which was prepared by dilution of a 1000 mg/L standard solution with 0.01–1.0 N HNO_3 or H_2SO_4 . Metal ion concentrations at equilibrium were determined by a Perkin–Elmer Optima 7000 DV inductively coupled plasma–optical emission spectrometer (ICP-OES). The percent sorption was calculated from the metal ion concentration in solution before and after equilibration.

RESULTS AND DISCUSSION

Poly(vinylbenzyl chloride)-bound pentaerythritol (PE) has three available $-\text{CH}_2\text{OH}$ groups. Reaction with diethyl chlorophosphate gave a neutral ester ligand with a high affinity for divalent

ions.¹¹ In the current research, the objective was to convert a $-\text{CH}_2\text{OH}$ group into one that could readily undergo nucleophilic reactions for further functionalization with a variety of reagents. In a first step, the conditions for the bromination of immobilized pentaerythritol were determined. The mechanism by which PBr_3 brominates alcohols is well known¹⁷ and summarized by eq. (1).



This was followed by conversion of the bromide to an amine for a study of metal ion affinities.



In the reaction of PE with diethyl chlorophosphate, only one of the hydroxyl groups was converted to the phosphate ligand over a range of conditions. To explore the extent of bromination, 2 g of PE were contacted with 0.10, 0.20, 0.25, 1.00 mL, and 2.50 mL PBr_3 to give an initial mole ratio of $[\text{Br}]$ to $[\text{pentaerythritol}]$ of 0.42, 0.83, 1.0, 4.1, and 10.4. Figures 1 and 2 show the FTIR spectra of PE and PE-Br (0.20 mL PBr_3 , 17 h). These spectra are compared with each other and with those of pentaerythritol $[\text{C}(\text{CH}_2\text{OH})_4]$,* dibrominated pentaerythritol $[\text{C}(\text{CH}_2\text{OH})_2(\text{CH}_2\text{Br})_2]$, and tetrabrominated pentaerythritol $[\text{C}(\text{CH}_2\text{Br})_4]$. It is found that the 1229/1209 cm^{-1} band region is due to brominated PE; the 1084/1047 cm^{-1} bands are due to

*Available on-line through the Spectral Database for Organic Compounds, maintained by the National Institute of Advanced Industrial Science and Technology (AIST), Japan. http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi. The FTIR spectrum for monobrominated pentaerythritol was unavailable.

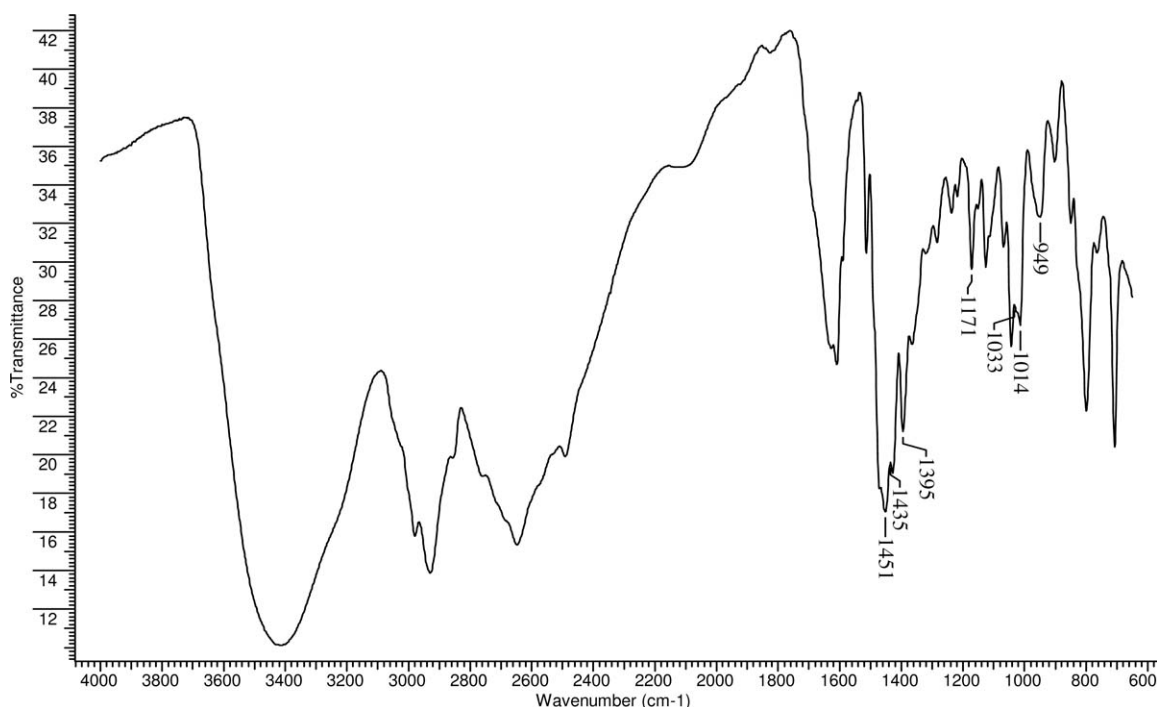
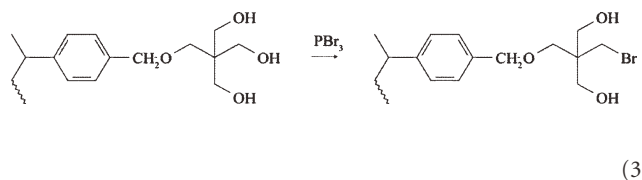


Figure 5. FTIR spectrum of diethylamine immobilized on polyVBC.

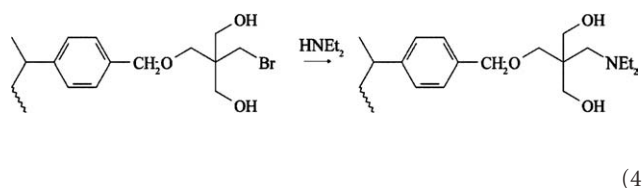
PE alone and they, based on the spectrum of $[\text{C}(\text{CH}_2\text{Br})_4]$, sharply diminish upon complete bromination. Both band regions will be present in partially brominated PE, as indicated by the spectrum of $[\text{C}(\text{CH}_2\text{OH})_2(\text{CH}_2\text{Br})_2]$. The effect of reacting PE with increasing amounts of PBr_3 on these bands is shown in Figure 3. Note that the 1229/1209 bands increase significantly with only 0.20 mL PBr_3 ; there is a further increase with 0.25 mL PBr_3 ; the increase is less pronounced with 1.0 mL but the distinct 1084 cm^{-1} band disappears; and with 2.50 mL PBr_3 , there is a further increase in the 1229/1209 bands. Comparing the bands at 8, 17, and 72 h reaction times shows the 1229/1209 region to grow as a function of time relative to the 1045 cm^{-1} region.

The bromine capacities were determined by elemental analysis to be 1.04, 2.70, 3.09, 3.97, and 4.30 for the PE-Br polymers prepared with 0.10, 0.20, 0.25, 1.0, and 2.5 mL PBr_3 , respectively. The theoretical bromine capacity is 3.05 for monobromination and 5.08 for dibromination. When the bromine capacities are combined with the FTIR spectra, it is concluded that there is monosubstitution up to 0.25 mL PBr_3 and that dibromination begins after that point. Comparing the initial mole ratios to the bromine capacities shows that all three bromines

in PBr_3 react. Complete bromination does not occur under the current reaction conditions and probably does not occur under any condition since brominating at reflux temperature produces the same FTIR spectra and bromine capacities. Further functionalization reactions were thus done with PE-Br prepared with 0.20 mL PBr_3 per 2 g PE to ensure an absence of dibromination [eq. (3)].



The utility of the brominated pentaerythritol for the synthesis of ion-complexing polymers was probed with its conversion to an amine-bearing polymer. Amines are complexants for metal cations¹⁸ and anions¹⁹ with applications in environmental remediation and hydrometallurgy. The complexation of the uranyl ion from acidic solutions is particularly important due to its application in uranium recovery processes.²⁰ PE-Br was thus aminated with diethylamine to give PE-N [eq. (4)].



Elemental analyses show a nitrogen capacity of 2.56 mmol/g and no bromine in the polymer. The nitrogen capacity is

Table I. Comparison of PE-N and NEt_2 Affinities for the Uranyl Ion

Metal	Acid conc N	%sorption PE-N	%sorption NEt_2
U(VI)	0.01 N HNO_3	36.4	1.33
U(VI)	1.0 N HNO_3	84.8	1.30
U(VI)	0.01 N H_2SO_4	79.4	8.42
U(VI)	0.1 N H_2SO_4	94.3	50.3
U(VI)	1.0 N H_2SO_4	76.4	19.2

Table II. Comparison of PE-N and NEt₂ Affinities for Divalent and Trivalent Ions

Metal	Acid conc. N	% sorption	
		PE-N	NEt ₂
Pb(II)	0.01 N HNO ₃	1.29	1.02
Cu(II)	0.01 N HNO ₃	1.86	1.72
Cd(II)	0.01 N HNO ₃	7.35	3.24
Zn(II)	0.01 N HNO ₃	5.46	3.08
La(III)	0.01 N HNO ₃	3.86	2.99
Lu(III)	0.01 N HNO ₃	5.04	1.93
Al(III)	0.01 N HNO ₃	2.39	5.26

consistent with the bromine capacity of the starting PE-Br (2.70 mmol/g). The FTIR spectrum (Figure 4) shows no bands at 1220/1209 cm⁻¹. This spectrum was compared to that of polyVBC-bound diethylamine (NEt₂, Figure 5). It has a nitrogen capacity of 4.00 mmol/g; when compared to the theoretical value of 4.27 mmol/g, the polymer is thus seen to be fully substituted. The FTIR spectra are similar with the only significant difference between the two being the 1045 cm⁻¹ band in PE-N associated with the —CH₂OH portion of the ligand. Results are consistent with monosubstitution and complete reaction at the —CH₂Br.

The binding ability of PE-N was probed with UO₂²⁺ in solutions of different HNO₃ and H₂SO₄ concentrations since results with soluble complexants show that the extent of complexation is dependent on both acid and acid strength.^{21,22} The complexation of the uranyl ion is determined from dilute (10⁻⁴ M) solution to focus on the inherent ion-ligand affinity in the absence of loading effects.^{23,24} As seen in Table I, PE-N has a high affinity for the uranyl ion from 1 N HNO₃ while the diethylamine polymer (NEt₂) has no affinity. The affinity for the uranyl ion by NEt₂ is greater from H₂SO₄ but it is far exceeded by PE-N. This mirrors results with soluble complexants since a higher affinity for uranyl sulfate relative to the nitrate has been observed with trioctylamine²⁵ and other amines.²⁶ Additionally, there is a maximum in affinity as a function of H₂SO₄ concentration and this has also been observed with the extraction of the uranyl ion by triisooctylamine in toluene;²⁷ it can be attributed to a combination of the species formed in solution and competition for the amine sites as the acidity increases.

The strong influence of the protons is evident in Table II wherein neither polymer has an affinity for divalent or trivalent ions from nitrate solutions at pH 2. The far greater affinity and selectivity of PE-N for the uranyl ion is thus found to be enhanced within the pentaerythritol environment and may be due to hydrogen bonding by the auxiliary hydroxyl groups to the uranyl oxygens. This is consistent with results from phosphorylated pentaerythritol and will be investigated further with FTIR spectroscopy.

CONCLUSIONS

The effect on metal ion sorption properties upon binding a tertiary amine site onto polyVBC through a pentaerythritol scaffold

is evident in the binding of the uranyl ion from acidic solutions. Further studies with the uranyl and other ions will focus on the mechanism of binding. Subsequent reports will extend the synthesis to further reactions of PE-Br and to phosphorylated PE as the starting material.

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