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Phosphoric Acid Ester Cation-Exchange Resins. 1. Synthesis and Preliminary Characterization†

Russell B. Selzer and Darryl G. Howery*

Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, New York 11210. *Received June 9, 1986*

ABSTRACT: Cation-exchange resins containing phosphoric acid ester functional groups based on a styrene/divinylbenzene copolymer matrix are synthesized. Functional groups are introduced onto the copolymer matrix by chloromethylation. Chloromethyl groups are converted to 2-hydroxyethyl groups through a series of reactions involving nucleophilic substitution with cyanide, hydrolysis, and reduction. Condensation phosphorylation of the chemically modified copolymer with pyridinium 2-cyanoethyl phosphate and monoethyl phosphate produces the phosphate monoester (PME) and phosphate diester (PDE) resins, respectively. The PDE resin is also prepared through condensation of the PME resin with ethanol. A preliminary characterization of the resins is formulated by measurements of capacities, pH titration curves, and stabilities. The PDE resin has a capacity of ca. 1.1 mequiv/g and contains monobasic exchange groups of moderately strong acidity. The PME resin exhibits two distinct capacities corresponding to stronger acid exchange sites (capacity ca. 1.1 mequiv/g) and weaker acid exchange sites (capacity ca. 1.1 mequiv/g). Both resins are shown to be stable to several cycles of acid, base, and salt treatments at 60 °C.

Introduction

According to the biological ion-exchanger model,[1] ion-exchange phenomena are considered to play a significant role in the functioning of the living cell. Synthetic ion-exchange resins are useful models for biological systems since they provide a particular functional group in a chemical environment free of the complexities inherent in living systems. In addition, the molalities of the counterions in synthetic resins (ca. 1–5 *m*) are similar to those in some living cells (ca. 1 *m*).[2] Thus, information on the behavior of isolated ion-exchange groups can serve as a basis for more general conclusions concerning complex biological systems.

An overall physicochemical characterization of important biological ion-exchange groups has been undertaken in our laboratory. The infrared spectra,[3] proton magnetic resonance spectra,[4,5] and electrical conductances[6] of sulfonic acid and carboxylic acid cation-exchange resins have been analyzed. Phosphate functional groups are also a major constituent of biological systems. Therefore, in order to develop comprehensive models for physiological processes, an understanding of the ion-exchange properties of phosphate groups is essential. However, suitable phosphate resins have not been available for extension of these studies.

Cation-exchange resins containing functional groups that are derivatives of phosphoric acid have proved difficult to prepare. The only well-characterized phosphorus-containing cation exchangers contain phosphonic acid functional groups.[7] These materials, containing carbon–phosphorus linkages, are of interest in relation to uranium recovery.[8,9] Recently, homogeneous polystyrene-based phosphinic and phosphonic acid resins have been prepared[10–12] for use as dual-mechanism bifunctional polymers, which extract metals by both redox and ion-exchange mechanisms. Previously reported phosphoric acid cation-exchange materials, characterized by carbon–oxygen–phosphorus linkages, include cellulose phosphate and phosphorylated poly(vinyl alcohol),[13–15] condensates of phenol, formaldehyde, and phenyl phosphate,[16] and triallyl phosphate polymers.[17] However, these substances were generally inhomogeneous and/or unstable with respect to hydrolysis of the phosphate functions from the polymer backbone.

We report here the synthesis of stable phosphoric acid cation-exchange resins suitable for detailed physicochemical characterization. The resins, based on a poly(styrene-*co*-2% divinylbenzene) matrix, contain functional groups that are esters of phosphoric acid. One exchanger, designated the PME resin for its phosphate monoester groups, is named poly(β-(4-vinylphenyl)ethyl phosphoric acid); the other, designated the PDE resin for its phosphate diester groups, is named poly(β-(4-vinylphenyl)ethyl ethyl phosphoric acid). Using the symbol R to represent the poly(styrene-*co*-2% DVB) backbone, we write the struc-

† Based on the Ph.D. Thesis of R.B.S., City University of New York, New York, 1982.

* To whom correspondence should be addressed.

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tures of these resins as PME = $RCH_2CH_2OP(O)(O^-M^+)_2$ and PDE = $RCH_2CH_2OP(O)(OCH_2CH_3)(O^-M^+)$, where M^+ is a monovalent counterion. We present methods for synthesizing the PME and PDE resins and report a preliminary characterization of the two resins involving measurements of capacities, phosphorus contents, pH titration curves, and stabilities.

Experimental Section

Chemicals and Apparatus. The styrene/2%-DVB copolymer starting material was generously supplied by R. Wheaton of Dow Chemical Co., Midland, MI. The reagents, chloromethyl methyl ether (Columbia Organics, Columbia, SC), titanium tetrachloride and sodium cyanide (Fisher Scientific, Fair Lawn, NJ), lithium aluminum hydride (Alfa Ventron, Danvers, MA), trichloroacetonitrile (Aldrich Chemical Co., Milwaukee, WI), and monomethyl phosphate and monoethyl phosphate (ICN Pharmaceuticals, Plainview, NY), were used without further treatment. The solvents (acetonitrile, tetrahydrofuran, ethanol, methanol, pyridine, and *N,N*-dimethylformamide, all purchased from Aldrich) were reagent grade.

2-Cyanoethyl phosphate, a phosphorylation reagent, was prepared after Tener.[18] About 0.7 L of dry ethyl ether (Aldrich), 35 mL of phosphoryl chloride (Pfaltz and Bauer, Stamford, CT), 55 mL of 3-hydroxypropionitrile (Aldrich), 65 mL of dry pyridine, and 350 g of barium acetate (Fisher) were used to produce about 100 g of barium 2-cyanoethyl phosphate dihydrate in a 40% yield. Conversion to the water-free pyridinium salt, suitable for use in the phosphorylation reactions, was accomplished as follows: 150 g of the barium dihydrate salt was dissolved in ca. 1.8 L of water with the aid of Dowex-50 (H^+ form, ca. 150 mL wet-bed volume) and mild heat. The solution was passed through a column of 0.7 L of Dowex-50 (H^+ form), which was then rinsed with 1.6 L of water. Pyridine (0.3 L) was added to the combined eluates, and the entire mixture (ca. 4-L total volume) was then concentrated by vacuum distillation at 25 °C to a volume of about 0.2 L, the trap vessels being cooled with liquid nitrogen. The concentrated solution was then lyophilized while several 50-mL portions of dry pyridine were added. Continued lyophilization resulted in a water-free viscous oil, which turned to a waxy solid in a freezer and then was dissolved in dry *N,N*-dimethylformamide for use in the phosphorylations.

The large-scale resin preparations were carried out in a 5-L three-neck flask equipped with a combination of thermometer, stirrer, reflux condenser, and pressure-equalized dropping funnel. Reactions were terminated by filtering the copolymer beads on a glass funnel and washing with the appropriate solvents. To prevent bead fracture, abrupt changes in solvent composition were avoided.

Analytical Methods. To monitor each stage of the conversion of the copolymer, small samples were withdrawn from the bulk of the particular reaction mixture and their infrared spectra recorded. The resin samples were washed and dried at 60 °C in a vacuum oven for 24 h. Potassium bromide (Fisher) disks were formed by mixing ca. 2 mg of resin and 200 mg of KBr in a steel ball mill for 2 min and pressing for 5 min under 50 tons in a 13-mm Wilks die. Spectra were recorded on a Beckman IR 18A or Perkin-Elmer IR-267 spectrophotometer.

The capacities of the product resins were determined by several techniques. The total capacity was found by equilibrating a weighed sample of dry H^+-form resin (ca. 1 g) with an excess of standard base (100 mL of 0.1 N NaOH) for 24 h in a covered flask, followed by back-titration of an aliquot with standard acid (0.01 N HCl). The total capacity was also determined by loading a weighed resin sample in a specific ionic form into a column, eluting the counterion, and quantitatively analyzing the eluate for the counterion. Thus, the H^+-form resin was treated with an excess of 1 M NaOH, 1 M KOH, or 0.5 M $Ca(NO_3)_2$ with some $Ca(OH)_2$ added, after which the resin beads were washed with several portions of progressively more dilute NaOH, KOH, or $Ca(NO_3)_2$ and then with a minimum of water (four 10-mL aliquots, each followed by forced-air drying to remove interstitial solution) to avoid hydrolysis. The resin sample was then treated with 250 mL of 1 M HCl, the eluate being collected in a volumetric flask. Sodium and potassium were determined by flame photometry (flame photometer from Process and Instruments Corp., Brooklyn, NY) and calcium was determined by atomic absorption (Perkin-Elmer Model 372 AA spectrophotometer).

The strong-acid capacity was found by treating a sample of H^+-form resin in a column with NaOH or KOH, followed by exhaustive washing with 6 L of water over a 2-day period. Metal counterions remaining on the resin were eluted with 1 M HCl and determined by flame photometry.

The phosphorus contents of the resins were found by application of the Schoniger oxygen-flask combustion technique.[19] Approximately 25 mg of dry resin (H^+, Na^+, or K^+ form, dried 1 day at 60 °C) was pulverized and weighed into a sample wrapper.[20] Combustion was performed in the presence of an absorbent solution composed of 10 mL of 0.09 M KCl. Fuming nitric acid (0.5 mL) was introduced into the flask just prior to combustion to minimize sparking. The phosphorus pentoxide combustion product was absorbed by shaking the flask intermittently for 1 h. The flask was then opened and washed down, and the contents were quantitatively transferred to a 150-mL beaker. The solution was evaporated to dryness over a steam bath, and the residue was redissolved in water and transferred to a 100-mL volumetric flask. This solution was analyzed for phosphorus (as orthophosphate) by the molybdiphosphoric acid visible spectrophotometric method.[21]

The pH titration curves for the H^+ forms of the resins were obtained by a standard technique.[22] Eight to fourteen resin samples were equilibrated for 4–7 days at 25 °C with varying amounts of standard base for each titration curve. In order that pK values for the resin acid groups could be estimated (see Results and Discussion), the titrations were carried out in 0.1 M NaCl.

Synthetic Methods

Overview of Resin Syntheses. The condensation phosphorylation method[23] is used to introduce phosphate groups onto the polymeric matrix. This method allows for better control of the type of phosphate ester linkages in the product, relative to direct phosphorylation methods utilizing phosphorus halides, which lead to cross-linking through phosphate groups and to polyfunctional products. The condensation approach requires the preparation of a polymer containing hydroxyl groups located in a suitable position on the functionalized polymeric network. The starting material is the well-characterized poly(styrene-*co*-2% DVB) copolymer.

In order to form the PME and PDE resins by condensation phosphorylation, the polymer alcohol must be poly(4-(β-hydroxyethyl)styrene-*co*-2% DVB), RCH_2CH_2OH. The preparation of RCH_2CH_2OH from the styrene/DVB copolymer consists of a series of five reactions. The sequence found to satisfactorily effect this conversion is shown in Figure 1. A one-carbon side chain is introduced onto the aromatic groups of the copolymer (I, R) by chloromethylation with chloromethyl methyl ether (CMME) and a Lewis catalyst, titanium tetrachloride. Through this reaction, a chloromethylated copolymer, poly(4-(chloromethyl)styrene-*co*-2% DVB) (II, RCH_2Cl), having a loading of chlorine functions higher than the loadings found in commercially available materials, can be secured. Introduction of a second carbon onto the copolymer side chain is readily accomplished by nucleophilic substitution of Cl on II by sodium cyanide in acetonitrile, producing poly(4-(cyanomethyl)styrene-*co*-2% DVB) (III, RCH_2CN). Hydrolysis of III with 70% sulfuric acid yields the carboxylic acid resin poly(4-(carboxymethyl)styrene-*co*-2% DVB) (IV, RCH_2COOH). Esterification of IV with ethanol/sulfuric acid produces poly(4-((ethoxycarbonyl)methyl)styrene-*co*-2% DVB) (V, $RCH_2COOC_2H_5$), which can be reduced with lithium aluminum hydride to the desired alcohol copolymer (VI, RCH_2CH_2OH).

The phosphoric acid cation-exchange resins are produced by condensation phosphorylation of VI in anhydrous

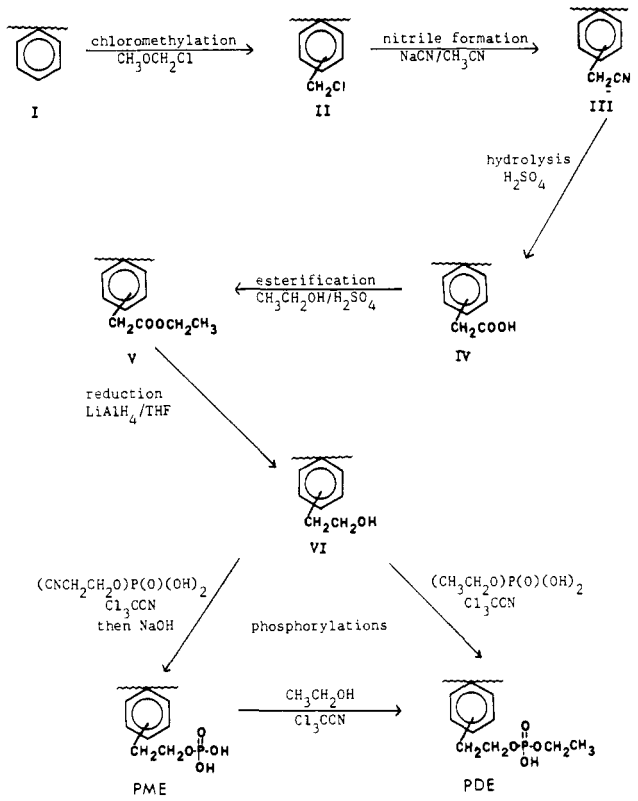

Figure 1. Synthetic sequence.

Table I
Characteristic IR Absorption Bands

polymer	freq, cm^{-1}	assignment
RCH_2Cl	1260	C–Cl overtone[25]
RCH_2CN	2250	C≡N stretch[26]
RCH_2COOH	1650–1700	COOH group[26]
$RCH_2COOCH_2CH_3$	1720	C=O stretch[26]
RCH_2CH_2OH	1030	C–O–H group[26]
$RCH_2CH_2OP(O)(OH)_2$	1000–1250	PO_4 group[26]
$RCH_2CH_2OP(O)(OCH_2CH_3)(OH)$	1000–1250	PO_4 group[26]

N,N-dimethylformamide, employing trichloroacetonitrile as the condensing agent. Reaction with monoethyl phosphate gives the PDE resin and reaction with 2-cyanoethyl phosphate produces an intermediate resin that readily loses the 2-cyanoethyl group under mildly alkaline conditions to form the PME resin. In an alternative method, the PDE resin can be synthesized directly from the PME resin by condensation with ethanol.

Details of Resin Syntheses. Application of these chemical reactions to the polymer system required the determination of the optimum reaction conditions for essentially complete transformation of the copolymer functional groups. Temperature, solvent, and reagent mole ratios were the significant variables considered. Sufficient swelling of the copolymer beads was critical to ensure maximum accessibility of the applied reagents to the reaction sites. Details of the small-scale experiments leading to the final reaction conditions reported below are described elsewhere.[24] Reactions were followed by measurement of the characteristic infrared bands of the functional groups, which are listed in Table I. The specific reaction conditions applied in each step of the synthetic sequence follow. The procedures apply to the reaction of about 0.5 kg of the styrene/DVB copolymer.

Chloromethylation. The starting material was in the form of 45–100-mesh beads. In the reaction apparatus, approximately 0.5 kg of the copolymer beads and 2 L of CMME were refluxed at 57 °C for 1 h. After the mixture cooled to 30 °C, the condenser was replaced with a pressure-equalized dropping funnel having an elongated glass stem that reached into the center of the flask below the surface of the reaction mixture. $TiCl_4$ (300 mL) was added from the dropping funnel over a period of 1.5 h. The reaction mixture was vigorously stirred throughout the process and the temperature was maintained at 30 °C by application of ice to the outside of the flask. At the completion of catalyst addition, the mixture was poured with stirring into a large beaker containing 3 L of 95% CH_3CH_2OH, breaking up any conglomerations of beads that may have formed. The alcohol was decanted, and the alcohol addition/decantation was repeated at least twice. The resin beads were transferred to a large sintered-glass funnel and washed with CH_3CH_2OH, CH_3OH, CH_3OH/4 M H_2SO_4, H_2O, and finally CH_3OH.

The conversion to RCH_2Cl was indicated by the appearance of a sharp, intense band at 1260 cm^{-1} in the infrared spectrum. This band corresponds to the first overtone of the C–Cl stretching vibration, which occurs in the 645–745-cm^{-1} range.

We attempted to quantify the mole percent loading of chloromethyl groups in the product resin by chlorine analysis. Application of the Schoniger oxygen-flask method, using KOH as the absorbent solution and potentiometric titration for chloride, gave inflated results for the chlorine loading. This was likely due to catalyst residues trapped in the copolymer beads (which were removed in the subsequent reaction steps).

Nitrile Formation. Reaction of RCH_2Cl with cyanide introduces an additional carbon onto the copolymer side chains. Application of this substitution reaction to the solid polymer system requires a medium of sufficiently low polarity to swell the beads but also of sufficiently high polarity to dissolve the reactant (NaCN) and product (NaCl) salts. Of the several solvent systems and reaction conditions tried, a 3:1 (v/v) mixture of CH_3CN and 95% CH_3CH_2OH was found to work best.

The RCH_2Cl resin was swollen for several hours in a minimum of CH_3CN and then reacted with 3 L of CH_3CN, 1.1 L of 95% CH_3CH_2OH, and 300 g of NaCN by maintaining the mixture at 90 °C for at least 24 h. Small samples of resin were withdrawn and washed with CH_3CN, H_2O, and CH_3OH. The IR spectra indicated product formation by the appearance of a sharp absorption band at 2250 cm^{-1} corresponding to the C≡N stretch and concomitant disappearance of the C–Cl band at 1260 cm^{-1}. The reaction was considered complete when no absorption at 1260 cm^{-1} was detectable. At this point, the beads were allowed to settle and the reaction solution was siphoned with caution while still hot. The beads were then transferred to a large glass funnel and washed extensively with CH_3CN, CH_3CH_2OH, CH_3OH, and H_2O. A small amount of TiO_2, trapped in the beads from the chloromethylation step, was removed in the next step.

Nitrile Hydrolysis. Hydrolysis of nitriles is usually accomplished with concentrated H_2SO_4. However, application of such solutions to polystyrene matrices may result in sulfonation of the polymer aromatic groups. Attempts to hydrolyze the nitrile resin with HCl or NaOH solutions were unsuccessful. Thus, hydrolysis with a sulfuric acid medium weak enough to prevent sulfonation was necessary. Acidic conditions were advantageous since any TiO_2 residues remaining in the beads were dissolved. A 5:1 (v/v) 70% H_2SO_4/CH_3CH_2OH solution was used to conduct the reaction.

Hydrolysis of the RCH_2CN resin involved heating the water-swollen copolymer for 20 h in a solution composed

of 1.8 L of concentrated H_2SO_4, 1.3 L of H_2O, and 0.5 L of 95% CH_3CH_2OH at 105 °C. The reaction was judged essentially complete when the IR spectrum of a sample exhibited no CN absorption band at 2250 cm^{-1}, this band being replaced by an extremely intense and somewhat broad carboxylic acid absorption at 1640–1720 cm^{-1}. Reaction was continued for 6 h beyond this point to ensure full conversion. The product was washed with H_2O and CH_3OH on a glass filter.

The product resin in this step, RCH_2COOH, is itself a weakly acidic cation exchanger, whose ion-exchange capacity could be utilized as a quantitative probe of the synthetic sequence. The fraction of functionalized aromatic groups (X) in the copolymer matrix is given by the formula $X = 104c/(1 - 58c)$, where c is the capacity of the carboxylic acid resin expressed as (grams of H)/(grams of dry resin). For three separate bulk resin samples, we obtained 0.44, 0.28, and 0.40 fractional loadings, respectively. None of the RCH_2COOH resins contained measurable chlorine, suggesting that all chloromethyl functions had undergone conversion and that all chloride-catalyst residues had been removed.

Esterification. The formation of RCH_2CH_2OH through direct reduction of RCH_2COOH with $LiAlH_4$ was not possible. Since esters of carboxylic acids are more easily reduced to the alcohols by $LiAlH_4$ than are the acids themselves,[27] it was necessary to esterify the carboxylic acid groups of RCH_2COOH before reduction to the alcohol resin. This conversion was accomplished by reaction with absolute CH_3CH_2OH and concentrated H_2SO_4. Attempts to esterify with dry CH_3OH failed.

After methanol wash, the RCH_2COOH resin was dried for 24 h at 70 °C. Esterification of the beads (swollen in CH_3CH_2OH) was conducted at reflux in 2.5 L of dry CH_3CH_2OH and 250 mL of concentrated H_2SO_4 for 20 h. The beads were washed with CH_3CH_2OH, H_2O, and CH_3OH. The product, $RCH_2COOC_2H_5$, exhibited a negligible ion-exchange capacity, based on the uptake of standard base. The conversion of the acid resin to the ester resin was accompanied by a change in the C=O absorption band in the IR spectrum, the broad peak ranging from 1640 to 1720 cm^{-1} in the acid-resin spectrum narrowing upon esterification to a sharp peak at 1725 cm^{-1}.

Reduction. The $RCH_2COOC_2H_5$ resin was reduced to the RCH_2CH_2OH resin by application of excess $LiAlH_4$ in tetrahydrofuran (THF). A relatively clear reductant solution was prepared by refluxing ca. 150 g of $LiAlH_4$ in 2.0 L of THF for 1 day, after which all solids were allowed to settle to the bottom of the flask. The clear supernate was poured directly into the reaction flask containing the ester-resin beads, which (after ether wash) had been dried at 70 °C for 2 days and swollen by refluxing in 1.5 L of THF for 1 day.

The reaction mixture was maintained at reflux for 48 h. Small samples were withdrawn, hydrolyzed, and washed, and their IR spectra were taken. A minimum absorption in the carboxyl regions (1150–1250 and 1650–1720 cm^{-1}) signified complete conversion. The product exhibited an intense IR band at 1030 cm^{-1} due to C–O and O–H stretching vibrations. After the reaction solution was decanted from the settled beads, the resin was added in small portions to a large beaker of cold 1 M H_2SO_4, with stirring. The hydrolyzed beads were then stirred for 1 day in 3:1 (v/v) 2 M H_2SO_4/CH_3CH_2OH. Treatment was completed by washing on a glass filter with 2 M H_2SO_4, 2 M NaOH, H_2O, and CH_3OH.

Analysis of the RCH_2CH_2OH resins gave 0.05, 0.03, and 0.03 mequiv/g, respectively, for the ion-exchange capacities. These small values indicate complete conversion (within the experimental error of the analysis, ±0.05 mequiv/g) of the carboxylic acid functional groups to hydroxyl groups.

Phosphorylations. The RCH_2CH_2OH resins were treated before phosphorylation by heating in 3:1 (v/v) 1 M NaOH/dioxane for 2 days and then in 3:1 (v/v) 1 M H_2SO_4/dioxane for 2 days. After thorough washing with H_2O and CH_3OH, the resins were dried for 2 days at 70 °C in a vacuum oven.

The general procedure for formation of the PME resin involved swelling the RCH_2CH_2OH resin (300 g) in 0.8 L of dry *N,N*-dimethylformamide (DMF) for 1 day. A quantity of pyridinium 2-cyanoethyl phosphate corresponding to a 3-fold mole excess over resin was dissolved in 0.6 L of dry DMF and added to the DMF-swollen resin. A 5-fold mole excess of trichloroacetonitrile (TCAN) over resin was then added, and the reaction mixture was stirred for 4 days at 65 °C. The resin was then filtered and washed with DMF, CH_3OH, and H_2O. The resulting $RCH_2CH_2OP(O)(OH)(OCH_2CH_2CN)$ resin was hydrolyzed to the PME resin by treatment with 2 L of 0.5 M NaOH at 50 °C for 1 day. Phosphorylation was indicated by the appearance of broad, intense phosphate-group absorptions between 1000 and 1250 cm^{-1} in the IR spectrum. The PME resins were conditioned with three cycles of 0.5 M HCl/H_2O/0.5 M $NaOH/H_2O$. The air-dried exchangers were sieved, the 40–70-mesh fractions being stored in the sodium form under water.

The PDE resin was prepared by swelling 300 g of RCH_2CH_2OH in 0.4 L of dry DMF for 1 day. A 2-fold mole excess of monoethyl phosphate in DMF was then added, and reaction was initiated by introduction of a 3-fold mole excess of TCAN. After reaction for 3 days at 65 °C, the resin beads were filtered and washed with DMF, CH_3OH, and H_2O. Conditioning with three cycles of 0.5 M HCl/H_2O/0.5 M NaOH, washing, and air-drying completed the workup. Phosphorylation was indicated by phosphate-group absorptions in the 1000–1250-cm^{-1} region of the copolymer IR. The 40–70-mesh beads were stored under water in the sodium form.

An alternative approach to the synthesis of the PDE resin, in which the polymeric phosphate monoester condenses with a simple alcohol (see Figure 1), was also used. Sixty grams of the PME resin was converted to the hydrogen form by treatment with 2 L of 0.5 M HCl, washed, and thoroughly dried at 70 °C for 2 days in a vacuum oven. The dry resin was swollen in 0.1 L of absolute CH_3CH_2OH, and 40 mL of TCAN with 80 mL of DMF was added. The mixture was stirred for 3 days at 65 °C, after which the filtered beads were washed with DMF, CH_3CH_2OH, and H_2O and conditioned as were the other resins. The direct conversion of the PME resin to the PDE resin was clearly shown in the spectral and capacity changes that ensued upon reaction. The broad absorption band between 1200 and 1220 cm^{-1} in the PME spectrum changed to a considerably sharper band at 1230 cm^{-1}, characteristic of PDE groups. Upon condensation with ethanol, a PME resin of capacity 1.80 mequiv/g in the dry hydrogen form yielded a product resin of capacity 0.92 mequiv/g, corresponding to the halving of the capacity expected on converting the dibasic PME exchange groups to monobasic PDE exchange groups. The IR spectrum and physical properties of this PDE resin were identical with those of the PDE resin prepared by the first phosphorylation method.

A measure of the extent of phosphorylation of the hydroxyl groups in the RCH_2CH_2OH resins was obtained by comparison of the mole fraction loading of the copolymer

(from the capacity data for the carboxylic acid resins) and the phosphorus contents of the product phosphate resins (see Results and Discussion). For the PME and PDE resins prepared in bulk syntheses, between 37 and 62% of the available hydroxyl groups were found to be phosphorylated.

Other Synthetic Approaches. Several other approaches to the synthesis of the desired resins were attempted.[24] The more promising of these focused on the introduction of oxyphosphorus groups onto a poly(4-(hydroxymethyl)styrene-*co*-2% DVB) matrix (RCH_2OH) and onto a poly(methacrylic acid) backbone. These experiments are briefly reviewed in this subsection.

Conversion of the styrene/DVB copolymer to RCH_2OH proceeds by refluxing RCH_2Cl with a 2-fold mole excess of potassium acetate in 2-methoxyethanol,[28] followed by hydrolysis of the resulting RCH_2COOCH_3 intermediate with NaOH in water/dioxane. On the basis of the reaction scheme of Abrams,[29] a direct route to the phosphate exchanger seemed feasible by phosphorylation of RCH_2OH with PCl_3 or $POCl_3$. Treatment of the RCH_2OH copolymer with PCl_3 would give a phosphodichloridite intermediate (RCH_2OPCl_2), which would be oxidized with H_2O_2 or Cl_2 and hydrolyzed to produce a phosphate exchanger. Treatment with $POCl_3$ in a manner similar to the phosphorylation of poly(vinyl alcohol)[30] and cellulose[31] would yield a phosphodichloridate intermediate, $RCH_2OP(O)Cl_2$, requiring only hydrolysis to form the final exchanger. All attempts at these direct phosphorylations with PCl_3 and $POCl_3$ (in a variety of solvents, e.g., CH_2Cl_2, dioxane, and C_6H_6 with added pyridine) failed to yield stable phosphorylated materials, the intermediate halophosphorus resins decomposing to RCH_2OH and inorganic phosphate upon aqueous hydrolysis. Instability of the benzyl phosphate linkages in the copolymer system is indicated by these observations.

Blackburn et al.[32] used pyridinium 2-cyanoethyl phosphate and dicyclohexylcarbodiimide (DCC) to prepare $RCH_2OP(O)(OH)_2$. We attempted a similar reaction scheme, and again, the phosphorus functions hydrolyzed from the copolymer matrix upon aqueous treatment. Condensation of RCH_2OH with 85% H_3PO_4 and DCC, a method employed in the phosphorylation of cotton,[30] and with urea phosphate and DCC[33] were also tested. In both cases, stable phosphorus-containing resins could not be prepared.

Merrifield[34] reported that, when employing polystyrene/DVB as a solid support in peptide synthesis, a stronger carboxy–ester linkage resulted when the aromatic rings of the copolymer were destabilized by introduction of various electron-withdrawing substituents, e.g., nitro and bromo groups. Bromination of RCH_2Cl with Br_2 and I_2 in CCl_4, followed by conversion of the Cl groups to OH groups as outlined above, gave an alcohol resin that, upon treatment with excess PCl_3 in dioxane/pyridine, did produce a stable phosphorylated material. This phosphorous acid monoester resin, whose IR spectrum displayed P=O absorptions in the 1000–1250-cm^{-1} region, had a capacity of 1.6 mequiv/g for the dry H^+ form. However, conversion of the phosphorous acid groups to phosphoric acid groups by oxidation with aqueous HNO_3 or Cl_2 was not successful.

Bio-Rex 70 (Bio-Rad Laboratories, Richmond, CA) is a poly(methacrylic acid) cation-exchange resin with a capacity of about 10 mequiv/g. Reduction of the carboxylic acid groups to hydroxyl groups would afford a copolymer that could form stable phosphate linkages upon phosphorylation. With this material, the benzyl phosphate ester instability is obviated, and phosphorylations could be carried out as for cellulose and poly(vinyl alcohol). Attempts to reduce the dry hydrogen form of Bio-Rex 70 with $LiAlH_4$ in THF failed, as did esterification of the carboxylic acid groups with ethanol and sulfuric acid. These results indicate that the copolymer matrix of Bio-Rex 70 restricts accessibility by these reagents to the carboxylate sites.

Table II
Capacities and Phosphorus Contents of the Resins

resin	total capacity,[a] mequiv/g	strong-acid capacity,[a] mequiv/g	% P[a,b]	P content,[c] mmol of P/g
PME-1	2.69	1.20	4.12	1.33
PME-2	2.30	1.13	3.41	1.10
PDE-1	1.00	0.95	3.40	1.10
PDE-2	1.26	1.20	3.95	1.27

[a] Based on the oven-dried (60 °C) H^+ forms. Experimental error in capacities ca. ±0.05 mequiv/g. [b] Average of five determinations. Experimental error ca. ±0.09%. [c] Based on % P.

Results and Discussion

A preliminary characterization of the PME and PDE cation-exchange resins was carried out by measurements of the cation-exchange capacities, phosphorus contents, and pH titration curves. In addition, some of the stability characteristics of the materials were ascertained.

Capacities. In Table II are listed the capacities and phosphorus contents for each of two samples of the PME and PDE exchangers (designated PME-1, PME-2, PDE-1, and PDE-2). Resin PDE-1 was prepared by phosphorylation of RCH_2CH_2OH with monoethyl phosphate and resin PDE-2 by direct conversion of resin PME-1 by condensation with ethanol. Comparison of the capacities and phosphorus contents for each of these resins provides direct experimental conformation of the nature of the functional groups in the two types of resins. For resins PME-1 and PME-2, the ratios of capacity (mequiv/g) to phosphorus content (mmol of P/g) are 2.02 and 2.09 mequiv/mmol of P, respectively. These data indicate two exchange sites per phosphorus atom, consistent with the presence of dibasic phosphoric acid monoester exchange sites. For resins PDE-1 and PDE-2, the capacity to phosphorus content ratios are 0.91 and 0.99 mequiv/mmol of P, respectively, indicative of monobasic phosphoric acid diester exchange sites.

Syntheses involving condensation of RCH_2CH_2OH with monomethyl phosphate (instead of monoethyl phosphate) produced PDE resins with unexpectedly high ratios of total capacity to phosphorus content, 1.3–1.7 mequiv/mmol of P. These data suggest that such PDE resins were polyfunctional, containing both monoester and diester phosphate groups as a result of partial hydrolysis of the methylalkyl portion of the phosphate diester groups. Again, the presence of one-carbon alkyl chains seems to lead to instability in the phosphate–ester linkages.

The PME resins exhibit two distinct capacities (second and third columns of Table II). The first corresponds to all of the exchange sites in the resin (total capacity), while the other applies only to the stronger acid exchange sites (strong-acid capacity). The total capacity was obtained by treating the H^+ form of the resins with excess standard base (pH > 11), while the strong-acid capacity was obtained by treating the H^+ form with an NaCl solution or by exhaustively washing the Na^+ form with water in a column until the effluent was neutral to phenolphthalein (pH < 6). When the Na^+ or K^+ form of the PME resin was washed with water in a column, a slow hydrolysis occurred, as revealed by an effluent that was basic to

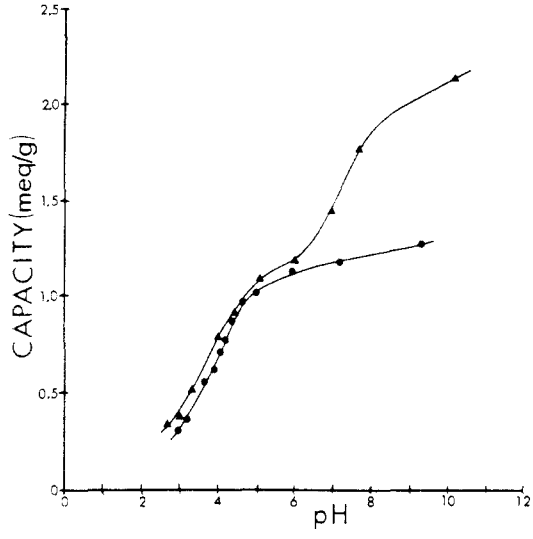

Figure 2. pH titration curves at 25 °C: (●) PDE resin; (▲) PME resin.

phenolphthalein. In the course of this hydrolysis, the salt form of the resin was converted partially to the proton form and hydroxide ions were generated. Complete hydrolysis of all weak-acid groups took about 2 days, with approximately 6 L of water being passed through the PME resin bed. The nonhydrolyzed exchange sites correspond to the stronger acid groups. The water hydrolysis of the fully loaded Na^+ or K^+ forms removed a quantity of alkali counterions equivalent to about 50% of the total capacity (see the third column of Table II). Hydrolysis did not occur for divalent ionic forms such as the Ca^{2+} form, suggesting stronger binding or complexation of such cations to the phosphate moieties.

These observations suggest a simple model for the PME exchanger groups entailing two distinct sets of exchange sites. The stronger acid exchange sites correspond to the first dissociation of protons on the PME groups and the weaker acid exchange sites correspond to the second dissociation of protons on the PME groups. Each set of exchange groups accounts for half of the total resin capacity. The exchange sites in the PDE resin are approximately equivalent to the stronger acid exchange sites in the PME resin.

The capacities of the resins were measured also in the Na^+, K^+, and Ca^{2+} forms. These capacities were obtained either by elution of the particular counterion from the fully loaded resin in a column with HCl or by combustion of the dry ionic form in the Schoniger flask followed by direct quantitative analysis for the cation and phosphorus. The total capacities of these ionic forms agreed with those given on the basis of the H^+ forms in Table II within 5% (e.g., for PME-2, mequiv of Na/mmol of P = 2.04 and for PDE-1, mequiv of Ca/mmol of P = 0.91). We conclude from the capacity data that the PME and PDE resins are homogeneous exchangers in which all of the phosphorus-bearing functional groups are available for counterion exchange.

Titration Curves. The pH titration curves measured in 0.1 M NaCl at 25 °C for a PME resin and a PDE resin are displayed in Figure 2. The curve for the PDE resin is characteristic of a monobasic acid, having one break at pH ≈ 4 that corresponds to the total capacity of the resin (≈1.2 mequiv/g). Similarly, the curve for the PME resin is characteristic of a dibasic acid, having two breaks. The first break at pH ≈ 4 corresponds to the stronger acid exchange sites (contribution to the capacity ≈ 1.1 mequiv/g) and the second break at pH ≈ 7 corresponds to the weaker acid exchange sites (contribution to the capacity ≈ 1.1 mequiv/g). These results are consistent with our model for the functional groups in the resins. The titration curves for the resins are not as sharp as those for monomeric acids. The gradually changing slopes are characteristic of polymeric acids and imply that exchange groups of a given type are only roughly equivalent, covering a range of acid strengths.

According to Helfferich's method,[35] the pK values of the functional groups in a cation-exchange resin can be calculated by relating the hydrogen ion concentration in the resin to the external pH. Helfferich's equation is

$$pK = pH + \log [Na^+] - \log \{[\bar{x}]/2\} \quad (1)$$

in which the pK of the functional groups is calculated from the external pH at half-conversion (obtained from the titration curve), the external Na^+ concentration (roughly fixed by titrating in 0.1 M NaCl), and the concentration of ionogenic groups at half-conversion ($[\bar{x}]/2$, calculated from the independently measured water content of the mixed Na^+/H^+ resin at half-conversion).

Application of eq 1 to our resins gives $pK_1 = 1.9$ and $pK_2 = 7.5$ for the PME resin and $pK = 2.5$ for the PDE resin. These pK values agree reasonably well with those reported for phosphate monoesters and diesters in solution.[36,37] The resin phosphate groups are only slightly less acidic than similar phosphate groups in solution, aqueous monoester phosphates having pK_1's in the 1.0–1.9 range and pK_2's in the 6.5–6.8 range and aqueous diester phosphates having pK's in the 1.3–1.7 range. These data indicate that the chemical environment of the phosphate groups is not significantly altered by the resin matrix in these materials. Similar comparisons for several phosphonates (containing C–P linkages) reveal much larger differences between the pK values for aqueous monoester phosphonates ($pK_1 \approx 1.8$ and $pK_2 \approx 7.1$)[38] and for several of the phosphonic acid ion exchangers (pK_1's in the 2.9–6.2 range and pK_2's in the 7.4–10.2 range).[39-42]

Stability. Since the capacity determinations and several other measurements on the resins were based on the oven-dried (ca. 60 °C) H^+ forms, the thermal stabilities of the resins were of interest. Samples of the H^+ forms of the PME and PDE resins were subjected to five repeated cycles of drying and rewetting, the drying being conducted for 24 h at 20 °C over P_2O_5 in a vacuum desiccator, at 60 °C in a vacuum oven, or at 120 °C in a vacuum oven. The samples dried at 20 and 60 °C displayed at most a 5% loss of capacity after five cycles, while no observable change occurred after one treatment cycle. Up to a 25% reduction in capacity was observed for the samples dried at 120 °C even after one treatment cycle.

The chemical stabilities of the H^+, Na^+, and Ca^{2+} forms were estimated by soaking the resins in 0.5 M HNO_3, 0.5 M $NaNO_3$, and 0.5 M $Ca(NO_3)_2$, respectively, for 48 h at 20 °C, followed by determination of the amount of phosphorus released into the solution phase. In all cases, phosphorus losses did not exceed 4%, the Ca^{2+} form being the most stable under these conditions. Stability with respect to repeated exchange cycles was estimated by subjecting the PME and PDE resins to five consecutive treatments with 0.5 M $NaOH/H_2O$/0.5 M HCl/H_2O. The ratio of the capacities before the first cycle and after the last cycle was 1.01 and 1.03 for a PME resin and a PDE resin, respectively. In a related experiment, a sample of the PME resin in a column was treated with aqueous $Mg(NO_3)_2$, followed by water rinsing and eluting with HCl. The eluted counterions were determined by atomic absorption, and after each of five consecutive treatments, the

counterion loadings remained constant within experimental error.

The phosphoric acid cation-exchange resins are reasonably stable under experimental conditions encountered in the course of additional characterization measurements to be reported in the accompanying[43] and subsequent[3] publications. In these papers, the water contents, ion-exchange selectivities, electrical conductances, and infrared spectra will be reported and interpreted.

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Miscibilities in Monodisperse Mixtures of Polystyrene, Poly(*p*-bromostyrene), and Their Copolymers

R. P. Kambour* and J. T. Bendler

Polymer Physics and Engineering Branch, Corporate Research and Development, General Electric Company, Schenectady, New York 12301. *Received April 1, 1986*

ABSTRACT: The phase behavior of cast films of mixtures of narrowly disperse polystyrene (I), poly(*p*-bromostyrene) (II), and their copolymers (III) was studied. Miscibility limits were characterized as functions of the degree of polymerization N and copolymer composition. The N dependence of x_c, the critical comonomer concentration of bromostyrene for phase separation in I–III mixtures, is accounted for with a simple mean field model (i.e., a composition-independent, positive segmental interaction parameter χ_{12} for the styrene–bromostyrene pair) for $0 < x_c < 0.4$ and $100 < N < 8000$. At $N < 100$ and $x_c > 0.4$, a downward drift in χ_{12} seems to emerge. Studies of I–III, II–III, and III–III mixtures, all at one N, also reveal a small reduction of χ_{12} with increase in average bromostyrene concentration in the blend. The size and magnitude of this dependence are rationalized in terms of enhanced coupling of the bromostyrene dipoles in the low dielectric medium afforded by blends of high styrene content. The composition dependence of χ_{12} is similar to that found in a study of the upper critical solution temperature behavior in a single I–III blend system of medium molecular weight described in the following paper. The combined results of these studies indicate that for high molecular weights as well as low molecular weights, the phase separations produced are related to upper critical solution temperatures.

The study of polymer–polymer blend miscibility from a fundamental viewpoint is made difficult by several problems, some of which are material in nature. One of the foremost is finding or producing a set of closely related blends, all of the members of which exhibit phase boundaries between their T_g's and their decomposition temperature.

A second problem arises from polymer chain length and chain length dispersity, both of which affect miscibility characteristics through the well-known combinatorial en-

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