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Methodology for Detecting Residual Phosphoric Acid in Polybenzoxazole Fibers

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Because of the premature failure of in-service soft-body armor containing the ballistic fiber poly[(benzo-[1,2-*d*:5,4-*d*′]-benzoxazole-2,6-diyl)-1,4-phenylene] (PBO), the Office of Law Enforcement Standards (OLES) at the National Institute of Standards and Technology (NIST) initiated a research program to investigate the reasons for this failure and to develop testing methodologies and protocols to ensure that these types of failures do not reoccur. In a report that focused on the stability of the benzoxazole ring that is characteristic of PBO fibers, Holmes, G. A.; Rice, K.; Snyder, C. R. *J. Mater. Sci.* 2006, *41*, 4105−4116, showed that the benzoxazole ring was susceptible to hydrolytic degradation under acid conditions. Because of the processing conditions for the fibers, it is suspected by many researchers that residual phosphoric acid may cause degradation of the benzoxazole ring resulting in a reduction of ballistic performance. Prior to this work, no definitive data have indicated the presence of phosphoric acid since the residual phosphorus is not easily extracted and the processed fibers are known to incorporate phosphorus containing processing aids. Methods to efficiently extract phosphorus from PBO are described in this article. Further, characterization determined that the majority of the extractable phosphorus in PBO was attributed to the octyldecyl phosphate processing aid with some phosphoric acid being detected. Analysis by matrix assisted laser desorption ionization of model PBO oligomers indicates that the nonextractable phosphorus is attached to the PBO polymer chain as a monoaryl phosphate ester. The response of model aryl phosphates to NaOH exposure indicates that monoaryl phosphate ester is stable to NaOH washes used in the manufacturing process to neutralize the phosphoric acid reaction medium and to extract residual phosphorus impurities.

The poly[(benzo-[1,2-*d*:5,4-*d*′]-benzoxazole-2,6-diyl)-1,4-phenylene] (PBO) fiber is part of a subclass of rigid-rod polymers known as polybenzazoles (PBXs). PBO evolved out of the pioneering research of Vogel and Marvel[1,2] on thermally stable polybenzimidazole (PBI), a related PBX polymer. Although PBO can be found in a variety of applications, this polymer was, until recently, used primarily in the manufacture of soft body armor (SBA) for civilian first responder applications, where its superior mechanical properties relative to polyaramids (e.g., Kevlar, Twaron)[3] ushered in the development of ultralightweight SBA.

PBO is prepared by the reaction of 1,3-diamino-4,6-dihydroxybenzene (DADHB) dihydrochloride with terephthalic acid (TA) in a reaction medium consisting of polyphosphoric acid (PPA) enriched with P_2O_5 as a dehydrating agent. Although the fibers have superior tensile strength and modulus, cut and abrasion resistance, and flame retardation relative to other high performance fibers, concerns have been expressed recently about the long-term stability of PBO fibers.[4] Several studies indicate a reduction in the mechanical properties of PBO (i.e., strain-to-failure, ultimate tensile strength) when exposed to moisture.[3,5] To better understand these concerns, the reaction scheme adapted from the research of So et al.[6,7] is shown in Figure 1, where the key feature in the PBO reaction is the formation of the benzoxazole ring structure. The influences of pH, ultraviolet (UV) radiation, and other factors on the stability of this ring have recently been reviewed by Holmes et al.,[8] with literature results indicating that the acid-catalyzed pathway to hydrolysis of the benzoxazole ring in PBO is feasible but pH sensitive.

In the reaction scheme shown in Figure 1, the carbonyl group in TA initially reacts with PPA to form a carboxylic-phosphoric mixed anhydride (species **A**). The hydroxyl groups of protonated DADHB, which are also in equilibrium with PPA as DADHB-PPA (aryl-phosphate) esters, react with the mixed anhydride to form esters (species **B**). Species **B** then undergoes the expected Railford acyl migration[8] to form an amide prior to the ring closure reaction that forms the benzoxazole ring (species **C**). Reaction of species **C**, 2,2′-(1,4-phenylene)bis(5-amino-6-benzoxazolol), with

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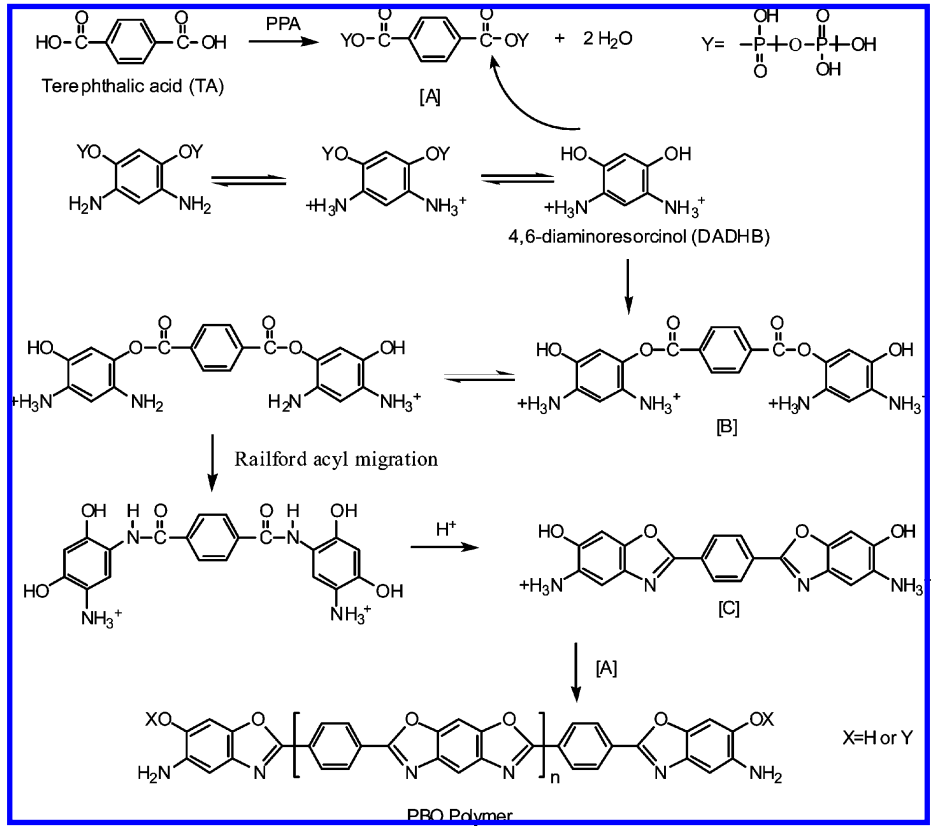

Figure 1. Reaction scheme for the preparation of PBO polymer (adapted from ref 6 1997 American Chemical Society and ref 7 1998 American Chemical Society).

species **A** leads to the formation of the PBO polymer where the PBO oligomers are preferentially capped with DADHB. The terminal DADHB groups have unreacted hydroxyl groups in the reaction medium that are in dynamic equilibrium (i.e., partially reacted) with PPA to form aryl-phosphate esters.

Elemental analysis indicates that processed PBO fibers have a residual phosphorus (P) mass fraction of approximately 0.3−0.4%.[3,4,9,10] This observation and the synthesis of PBO in PPA have led many researchers to make the plausible assumption that the residual phosphorus in PBO fibers is due to phosphoric acid (PA) and to infer that PA catalyzes the mechanical property degradation observed in PBO fibers. This assumption is based on the research of Jackson et al.[11] who showed that under acidic conditions simple benzoxazoles hydrolyze principally to the corresponding amidophenols. Two research reports[4,5] provide indirect evidence of the PA catalyzed hydrolysis reaction. In reference 5, the tensile strengths of PBO fibers are found to decrease when the phosphorus mass fraction is increased above 1% by exposing the fibers to increasing amounts of phosphoric acid. In the manufacture of PBO fibers, a residual phosphorus level between (2000 to 5000 mg/kg) is generally targeted.[12] This is particularly important when one observes that the severe conditions achieved by exposing PBO fibers to phosphoric acid are unlikely to be encountered in normal applications.

Furthermore, it is noted that extreme washing treatments (boiling water or Soxhlet extraction) are not effective in lowering the phosphorus content in as-spun dried or heat treated fiber samples. Research by others[9] indicates that the residual phosphorus mass fraction in PBO fibers can be reduced from 0.4% mass fraction to just 0.25% mass fraction by washing the fibers with supercritical carbon dioxide. Finally, a recent investigation performed at the National Institute of Standards and Technology (NIST) exposed soft body armors composed of PBO fibers to a constant hydrolytic environment for 6 months. Consistent with previous research, chemical degradation of the fibers was observed by difference Fourier transform-infrared (FT-IR) spectroscopy.[10]

All extant research[3−5,10] indicates that PBO fibers are degraded by hydrolytic action, which researchers presume to be catalyzed by residual PA. Complicating this seemingly straightforward interpretation is the absence of direct evidence for the existence of PA in processed PBO fibers and the knowledge that alkyl-phosphate esters are often used as processing aids during the manufacture of PBO fibers. Therefore, the research in this article will focus on the development of a direct approach for identifying phosphoric acid in the presence of alkyl-phosphate esters that may be present and to provide additional insight as to the nature of the seemingly nonextractable phosphorus found in PBO fibers.

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In this article, X-ray fluorescence (XRF) spectrometry along with standard derivatization procedures, extraction techniques, and model compounds are used to develop a coherent approach for interrogating PBO fibers for the presence of residual phosphoric acid compounds. Because of the insolubility of PBO oligomers and prepolymeric species in most solvents, matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) is also employed to identify species in polymer oligomers. A dual injector gas chromatograph/mass spectrometer (GC/MS) is used in electron impact (EI) and chemical ionization (CI) modes to obtain fragmentation spectra and molecular ion data for extracted low molecular mass species. To unequivocally identify extracted phosphorus compounds, a parallel flame photometric detector (FPD) and a nonparallel nitrogen phosphorus detector (NPD) are also used.

EXPERIMENTAL SECTION

Materials. 2,2′-(1,4-phenylene) bis(benzoxazolyl) (AF1), 2,6-diphenylbenzo[1,2-d;5,4-d′]bisoxazole (AF2), and 2-phenylbenzoxazole (AF3), model compounds of PBO, were supplied by the Wright Patterson Air Force Research Laboratories (see ref 13 for details). PBO fibers were obtained from a field returned vest supplied by the Department of Justice. Phosphoric acid, phosphorus pentoxide, 2-phenylbenzoxazole (PBOm), 4,6-diaminoresorcinol (DADHB), 2-aminophenol (2-AP), terephthalic acid (TA), trimethyl phosphate (TMP), triphenyl phosphate (TPhP), sodium phenyl phosphate dibasic dihydrate (DNaPhP), sodium hydroxide, and concentrated hydrochloric acid (HCl, 37% mass fraction) were purchased from Aldrich Chemical Co. and used as received. (Certain commercial products and equipment were named in this paper for the purpose of adequately specifying the experimental conditions and the sources of analytical results. Such descriptions do not constitute endorsement by the National Institute of Standards and Technology, nor do they imply that the equipment and products are necessarily the best for the purpose.) HCl used in this study has phosphorus (P) < 0.01 mg/kg (Fluka data).

Synthesis of PBO Oligomer. The synthesis method was adapted from refs 14 and 15. In this study, 2-AP was added as an end-capping material to keep the molecular mass of the PBO oligomer in a range that could be analyzed by MALDI-TOF MS. Poly(phosphoric acid) was prepared by the following method. Phosphorus pentoxide (500 g) was added slowly to 196 mL of 85% PA while the mixture was stirred under nitrogen. The mixture was then heated at 150 °C overnight to yield a homogeneous (clear) solution of PPA.

After the temperature of PPA was decreased to 80 °C, 5.00 g (0.0235 mol) of DADHB and 0.51 g (0.0047 mol) of 2-AP were added under a slow stream of nitrogen, and the mixture was heated at 80 °C for 16 h. Then the mixture was heated at 110 °C for 8 h until the evolution of HCl ceased. Terephthalic acid (TA) in the amount of 4.29 g (0.0258 mol) was added, and the mixture was heated at 150 °C for 12 h followed by 175 °C for 4 h. The brown solution was poured into water and washed with distilled water and dried. The oligomer was then washed 10 times with 1 L aliquots of 52 °C water, dried, and rewashed 10 additional times with 1 L aliquots of 75 °C water.

1st Soxhlet Extraction of 1st PBO Fibers. A total of 10 g of PBO fibers (1st Fiber as received) were placed in a thimble made from filter glass, which is loaded into the main chamber of the Soxhlet extractor. About 1 L of distilled water was used as the extraction solvent and was refluxed for 7 days. This was done to remove all loosely bound phosphorus-containing species and additives. The fibers were tested using XRF before and after the extraction procedure to determine the amount of removed phosphorus. The extraction fluid was placed in an oven at 52 °C and reduced in volume to about 10 mL. This fluid (1st Water Extract of 1st Fiber) and a blank of water run through the same Soxhlet extraction and evaporation procedure were analyzed by XRF and GC/MS.

1st Soxhlet Extraction of 2nd and 3rd PBO Fibers. The same procedure described above was repeated with the 2nd and 3rd sets of PBO fibers, which were from different manufacturing lots. Samples derived from the Soxhlet procedure are labeled as follows: 2nd Fiber as received, 1st Water Extract of 2nd Fiber, 1st Extract Fiber of 2nd Fiber, 3rd Fiber as received, 1st Water Extract of 3rd Fiber, and 1st Extract Fiber of 3rd Fiber.

Soxhlet Extraction of PBO Oligomers. Synthesized PBO oligomers were also extracted by the Soxhlet procedure described above for 14 days and analyzed by XRF, MALDI-TOF MS, and GC/MS.

2nd Soxhlet Extraction of 1st PBO Fibers. A 7.8 g quantity of the extracted PBO fibers (1st Extract Fiber of 1st Fiber) was placed between sheets of weighing papers (VWR Scientific Products) and then crushed with a mortar and pestle chilled using liquid nitrogen to help expose the microscopic voids found in PBO fibers (see Figure 2) to the water extractant. These crushed fibers were then extracted for 14 days with 800 mL of distilled water by the Soxhlet procedure described above. Phosphorus content in the fibers was monitored by XRF analyses before and after the second Soxhlet extraction. The final extracted fiber was labeled as 2nd Extract Fiber of 1st Fiber. The extractant was concentrated to 15 mL. Fibers (2nd Extract Fiber of 1st Fiber) and the extractant (2nd Water Extract of 1st Fiber) were analyzed by MALDI-TOF MS and GC/MS to identify the species removed from the PBO fibers.

1st Caustic Treatment on 2nd Extract Fiber of 1st Fiber. A 3.54 g portion of the 2nd Extract Fiber of 1st Fiber was refluxed in 1 L of 0.1 mol/L NaOH solution for 7 days. After cooling down, the fibers (1st Caustic treated Fiber of 1st Fiber) were separated from the solution and dried in air. The solution (1st Caustic solution of 1st Fiber) was concentrated in the 52 °C oven to 10 mL. XRF measurements were done before and after the 1st Caustic treatment.

2nd Caustic Treatment on 1st Caustic Treated Fiber of 1st Fiber. A 3 g quantity of 1st Caustic treated Fiber of 1st Fiber was refluxed in 1 L of 1 mol/L NaOH for 7 days. Fibers (2nd Caustic treated Fiber of 1st Fiber) were separated and dried in air. The solution was concentrated in air to about 100 mL then acidified with concentrated HCl to approximately pH 4. NaCl and SiO_2 precipitated during acidification and were removed by

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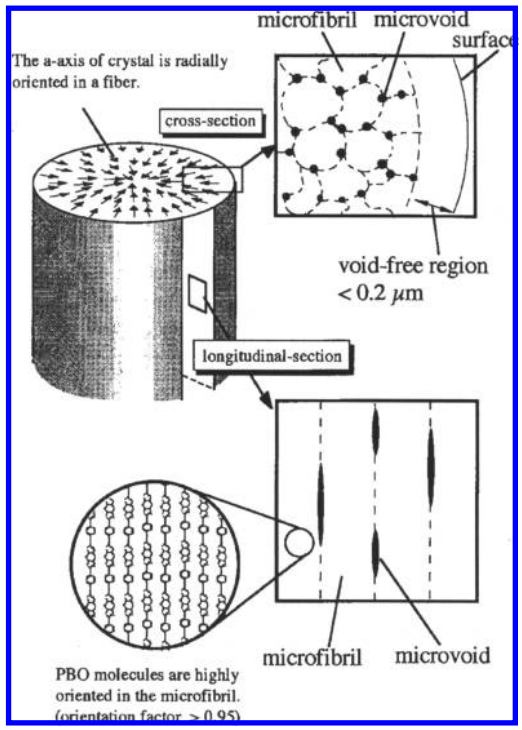

Figure 2. PBO structure model of AS fiber. (Reprinted with permission from ref 15. Copyright 1998 Wiley).

filtration. The acidified solution was concentrated to 10 mL. Salts precipitated during concentration were removed by filtration. Fibers before and after this caustic treatment were analyzed by XRF. The concentrated solution (2nd Caustic extract solution of 1st Fiber) was analyzed by GC/MS after methylation.

1st Caustic Treatment on 2nd PBO Fibers. The same caustic extraction procedure was applied to the 1st Extract Fiber of 2nd PBO fibers. Samples were labeled 1st Caustic extract solution of 2nd Fiber and 1st Caustic treated Fiber of 2nd Fiber.

Test of Stability of Chemically Bound Nonextractable Phosphorus. One of the two theories that have been advanced to explain the nonextractable phosphorus in PBO fibers suggests that the phosphorus is chemically bound to the polymer as aryl-phosphate esters. These aryl-phosphate esters in the final product are thought to arise from the known equilibrium reaction of PPA with the unreacted hydroxyl groups of DADHB (Figure 1), with the NaOH neutralization and washing procedure not affecting their complete removal. Interestingly, literature results indicate that phenyl phosphates can be hydrolyzed under the caustic conditions that are normally used to wash the process fibers. Triphenyl phosphate (TPhP) and sodium phenyl phosphate dibasic dihydrate (DNaPhP) were used as model compounds to test the stability of aryl-phosphate esters exposed to caustic materials.

A mass of 11.3 mg of TPhP was added to 28 mL of 1 mol/L NaOH solution in a single neck, 100 mL round-bottom flask equipped with a condenser. The mixture was refluxed for 7 days. This mass of TPhP corresponds to 1.1 mg of phosphorus. According to XRF results, 8.9 mg of P is present in 3.54 g of PBO fiber after two aqueous Soxhlet extractions and treatment of these fibers with a 0.1 mol/L NaOH solution. Under the test conditions, TPhP melted during boiling but remained immiscible with water. The contents of the flask were acidified by adding concentrated HCl after cooling. Precipitated solids (remaining unreacted TPhP, NaCl, and SiO_2 were removed by filtration, and the remaining solution was concentrated to 10 mL. Salt generated during the concentration was removed by filtration and then extracted with diethyl ether for analysis by GC/MS. The concentrated diethyl ether extract and the concentrated solution were modified by the methylation procedure for further analysis.

The same caustic treatment procedure was performed on 7.56 mg of sodium phenyl phosphate dibasic dihydrate (DNaPhP) in 28 mL of 1 mol/L NaOH. DNaPhP was soluble in caustic water. The solution was acidified and concentrated to 10 mL after boiling for 7 days. Solids precipitated during the procedure were removed by filtration. An aliquot of 0.5 mL of the concentrated solution was modified by methylation for GC/MS analysis. This procedure was repeated on 10.4 mg of sodium phenyl phosphate dibasic dihydrate in 38 mL of 1 mol/L methanol $NaOCH_3$ solution.

UV Irradiation. UV irradiation was performed with an apparatus equipped with a 1000 W xenon arc lamp (Oriel Corp). A 4.98 g quantity of 1st Caustic treated Fiber of 2nd Fiber was dipped into 200 mL of acidified water (pH 4) and divided into three portions. Each sample was placed in a wide-mouth beaker which was placed horizontally in the Oriel apparatus. Light intensity at the sample site was measured with a Newport Radiant power meter and probe, models 70260 and 70268, respectively. The light intensity at the sample was about 950 W/m^2. Each portion was exposed to UV radiation with no filters for 25 h, during which the acidified water was replenished by adding 50 mL every 8 h to prevent the sample from going to dryness (open container approach). After the UV irradiation, the fibers were gathered from the beaker, squeezed to remove liquid, and dried in air. The liquid was concentrated to 21 g, and then 1.7 g was methylated to facilitate GC/MS measurement.

A second procedure was performed in a sealed poly(methylmethacrylate) (PMMA) chamber having removable quartz windows to allow for loading and unloading of test specimens and transmission of UV radiation.[13] The top of the PMMA container was fitted with two poly(tetrafluoroethylene) screw stoppers to facilitate injection and extraction of liquid. Three grams of 2nd Caustic treated 1st Fiber, 400 mL of acidified water (pH 4), and a magnetic stirring bar were placed in the sealed chamber. The chamber was subsequently exposed to unfiltered UV radiation for 7 days while stirring. The fibers were removed from the chamber and filtered with a Buchner funnel with filter paper (Whatman). The filtrate was concentrated to 10 mL, methylated, and then analyzed by GC/MS. The amount of phosphorus in fibers before and after UV treatment was analyzed by XRF.

The sodium phenyl phosphate dibasic dihydrate (DNaPhP) compound was also subjected to UV irradiation. A quantity of 12.7 mg of DNaPhP was put into 12.5 g of acidified water (pH 4) in a quartz container, which was then sealed with a Teflon stopper (sealed container approach). The contents were exposed to UV radiation with no filters. Aliquots of 0.5 mL were taken from the container after 0, 2, 12, and 24 h for methylation and GC/MS analysis.

Methylation Methods. The Soxhlet extracts were methylated using an in situ consumption diazomethane generator.[13] The generator is composed of three test tubes arranged in a stair-step fashion with test tube 1 being the highest in the arrangement.

Since diazomethane presents an explosion hazard, the safety precautions listed in ref 13 were followed.

A quantity (10 mL) of peroxide-free diethyl ether was added to test tube 1, and the nitrogen pressure was adjusted to give a smooth bubbling in test tube 1. A mixture of about 4 mL of a 37% mass fraction KOH solution in distilled water and 6 mL of carbitol was added to test tube 2, and again the nitrogen pressure was adjusted to give a smooth bubbling in test tubes 1 and 2.

Approximately 1 mL of each concentrated aqueous extract along with 5 mL of diethyl ether/ethanol (3:1) mixture were added to test tube 3. The diethyl ether/ethanol mixture was used rather than diethyl ether alone to provide a homogeneous mixture with the aqueous solution. Earlier research[16] supports this approach since diazomethane reacts with water to form methanol. Again the nitrogen pressure was adjusted to yield uniform bubbling in all three test tubes. Approximately 1.0−1.5 g of diazald was added to test tube 2. After 6 min, additional diazald was added to test tube 2, and the reaction was continued until the sample in test tube 3 turned yellow, indicating the complete reaction of labile protons. Nitrogen was then blown over the sample in test tube 3 to evaporate residual solvents.

The solid flakes that were observed on the PBO fibers after boiling them in NaOH were also methylated after the following sample preparation. The solids were dissolved in an 80:20 mixture of 3:1 ether/ethanol mixture with H_2O. This combined mixture of ether, ethanol, and water was acidified with concentrated HCl and methylated as described above.

Measurements. *LDI- and MALDI-TOF MS.* Mass spectra were obtained using a Bruker Daltonics (Billerica, MA) REFLEX II spectrometer. The acceleration voltage was 25 kV, and the reflectron mode was used. Delayed extraction was 0.750 μs. A nitrogen laser at 337 nm was employed as a source. External mass calibration was performed using CsI_2. The resolution of the instrument is 20 000 atomic mass units (amu).

Samples were prepared by the following methods. For solid samples such as AF1, AF2, AF3, PBOm, and PBO oligomer, a small quantity of sample was ground with 20 μL of THF/HCl mixture (2 mL/1 drop) using a mortar and pestle until most of the solvent evaporated. The sticky sample for doing LDI-TOF-MS was pressed using a spatula onto the stainless steel substrate which was covered by Parafilm. For liquid samples such as extracts, 1 mL was concentrated in an oven at 52 °C. Samples were prepared using a variety of matrix/salt conditions: THF/HCl mixture (2 mL/1 drop), acetonitrile/0.1% of TFA solution (1:1 by volume), and sinapinic acid in THF (10 mg/mL)/Na TFA in THF (10 mg/mL) (1:1 by volume). Prepared samples were spotted onto a stainless steel plate and air-dried.

GC/MS. All methylated aqueous solutions were concentrated to approximately 0.5 mL. The methylated products were then extracted into about 3 mL of diethyl ether. The diethyl ether solution was then concentrated to approximately 1 mL. These concentrated samples were then analyzed by GC/MS with the specific equipment being a dual injector Trace GC 2000 gas chromatograph interfaced to a Trace DSQ II mass spectrometer (MS, Thermo Finnegan). The resolution of the instrument is 1 200 amu. The GC was also equipped with a flame photometric detector (FPD) and a nitrogen/phosphorus detector (NPD). The GC is equipped with a split/splitless (S/SL) injector and a programmable temperature vaporizing (PTV) injector. The effluent from a 15 m × 0.25 mm i.d. × 0.25 μm Rxi-5MS capillary column attached to the PTV injector was split to the FPD and MS using a MS-column flow splitter (SGE Analytical Science). This device equalizes the retention times between the FPD and MS detectors, thereby allowing for phosphorus containing compounds to be distinguished in the GC/MS chromatogram. A second 15 m × 0.25 mm i.d. × 0.25 μm Rxi-5MS capillary column attached to the second injector (S/SL) and connected directly to the NPD detector provides additional information about phosphorus containing compounds. Sample volumes of 1 μL were injected with splitless mode. Helium was the carrier gas (flow rate, 1 mL/min). The oven was programmed with an initial temperature of 50 °C and a hold time of 1 min. The GC oven temperature was raised 20 °C/min up to 260 °C and held at 260 °C for 10 min. The DSQ II mass spectrometer acquired electron impact (EI) and/or chemical ionization (CI), full scan data with a mass range of 50−600 u, where 1 u = 1 g/mol.

XRF. Fiber samples, liquids, and key ingredients in the synthesis and extraction experiments were analyzed by XRF to detect elements present, other than H, C, O, and N, and to determine the approximate mass fractions of those elements. The results are presented in Table 1. Because the experiments were viewed as investigative in nature, it was decided to emphasize speed and comparability over expensive and time-consuming quantitative methods. This is justified because the experiments were expected to cause substantial changes in composition or no changes at all. Fundamental parameters (FP) XRF methods are well suited to this purpose. The investigator can specify *a priori* knowledge of the chemical and physical properties of each specimen. The FP XRF program used in this work was the IQ+ method from PANalytical, Inc. (Almelo, The Netherlands), which was run on a PANalytical model PW2404 wavelength-dispersive spectrometer. The method was calibrated using a set of glass and briquette standards provided by the vendor, bolstered by a number of NIST Standard Reference Materials. All specimens were weighed into sample cells (25 mm polyethylene with 6 μm polypropylene window), and an estimate of the viewed area was made. The mass and area values were entered into IQ+ to scale the expected X-ray count rates calculated from the FP equations. PBO fibers were specified as having a chemical formula of $C_{14}H_{10}N_2O_2$, which was chosen as the balance compound because FP methods solve a set of equations with the SUM = 100% constraint. Similarly, aqueous solutions were specified with H_2O as the balance compound, and white flakes found in some fibers were specified with $C_6H_{10}O_5$ (a general formula for cellulose from filter paper) as the balance compound. In nearly all cases, the inorganic elements were calculated as the elements. In materials that were mostly inorganic solids, metals were usually specified as oxide compounds. Measurements were made in vacuum for solids or in He for liquids, with the Rh anode X-ray tube operated at 3 kW.

The performance of IQ+ is "semiquantitative" in that it varies from quantitative for well-controlled specimens to "order of magnitude" results, when specimens are difficult to handle, of very small quantity, or have other complicating properties. XRF methods are at their best when specimens share the same physical

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Table 1. Selected X-ray Fluorescence Results for PBO Fibers, Model Oligomers, and Liquids[a]

	elements								
fiber samples	Na	Al	Si	P	S	Cl	K	Ca	Fe
1st Set of Fibers									
PBO fibers as received	0.31	0.002	0.007	0.38	0.004	0.047	0.012	0.040	
PBO fibers after water wash	0.19	0.005	0.022	0.28	0.003	0.008	0.010	0.005	0.002
PBO damaged (by grinding)	0.20	0.013	0.009	0.30	0.004	0.007	0.010	0.009	0.029
PBO treated with 0.10 mol/L NaOH	8.6	0.033	1.7	0.25	0.002	0.009		0.006	0.006
PBO treated with 1.0 mol/L NaOH	0.45	0.065	0.49	0.25		0.008		0.029	0.017
flakes from NaOH treated fibers[b]	1.8	0.14	18	0.020		2.0		0.010	0.040
fibers after removing flakes	0.58	0.038	0.71	0.28	0.008	0.012	0.010	0.024	0.005
fibers after UV irradiation (open)	0.16	0.005	0.20	0.26		0.023		0.002	0.004
2nd Set of Fibers									
PBO fibers as received	0.20		0.004	0.32	0.001	0.014	0.040	0.005	0.033
PBO fibers after water wash	0.12	0.009	0.012	0.29	0.002	0.011		0.013	0.03
PBO treated with 1.0 mol/L NaOH	0.45	0.035	0.34	0.27	0.003	0.014		0.009	0.007
fiber after UV irradiation (closed)	0.052	0.025	0.69	0.21		0.064			0.002
3rd Set of Fibers									
PBO fibers as received	0.15		0.005	0.24	0.003	0.008	0.024	0.003	0.002
PBO fibers after water wash	0.20		0.003	0.25	0.001	0.007		0.003	0.021
PBO Model Oligomers									
before extraction		0.008	0.016	1.4		0.027		0.010	0.013
after extraction		0.003	0.004	0.062	0.001	0.12		0.002	0.013
treated 0.10 mol/L NaOH	0.61	0.020	0.12	0.036	0.001	0.10		0.19	0.034
Liquid Samples[c]									
blank solvent[d]	0.043	0.009	0.27	0.024	0.001			0.010	
extract from damaged fibers	0.034	0.021	0.50	0.026	trace[e]		0.006	0.002	
extract from PBO model oligomers	0.038		0.16	0.80				0.010	

[a] All values are mass fraction (%). Uncertainty: For P, the uncertainty (approximately 95% confidence level) is +10% to −50%. For other elements, differences >100% may be significant. PBO polymer fibers were modeled as $C_{14}H_{10}N_2O_2$. [b] Flakes were modeled as cellulose $C_6H_{10}O_5$ because they contain weighing paper. [c] Liquid samples were modeled as H_2O with P as PO_4 and S as SO_3. [d] A blank cell means the element was not detected. [e] A note "trace" indicates the element was detected but was <0.001%.

characteristics, viz., the same size, shape, and mass and when all constituent elements can be measured. PBO fibers and small quantities of powder are less than ideal because the fibers are springy and do not lie flat. Water and organic materials are mostly C, N, and O, which cannot be measured when the specimen is placed inside a cell. Fluorescent X-rays from these elements cannot penetrate the thin polypropylene window supporting the specimen at the bottom of the cell.

The uncertainty of XRF results was evaluated by analyzing specimens of SRM 1575a Pine Needles, which contains 0.107% total P. Measured results for P in SRM 1575a ranged from quantitative when sufficient sample mass was provided to biased low by approximately 35% when the sample mass was only 20 mg. The results for other elements present in SRM 1575a were observed to be biased either high or low by amounts ranging from 50% to a factor of 10 depending on the mass of sample, the element, and the energy of the X-ray line measured for that element. On the Certificate of Analysis, it is recommended to use at least 250 mg of SRM 1575a for a determination. In addition, quantities <100 mg did not cover the entire viewed area of the specimen cup, and results were low because P K-$L_{2,3}$ X-rays are of low energy and do not penetrate deeply into most materials. Therefore, samples of low mass and uneven distribution in a cell are expected to yield biased results. This source of bias is expected to affect the PBO and other samples studied in this work. The results for P reported in Table 1 have been assessed an overall relative uncertainty based on a nonsymmetrical, triangular distribution of + 10% to − 50% relative (approximate 95% level of confidence) based on the observed performance for SRM 1575a. However, comparisons of values in Table 1 should be viewed in the context of the expected repeatability of measurements for the IQ+ method. On the basis of past performance of the method, the relative standard deviation for repeatability is approximately 10%. The additional elements reported in Table 1 are provided for forensic purposes. For each element, differences of a factor of 2 or greater may be significant.

RESULTS AND DISCUSSION

On the basis of the nomenclature used in prior accounts,[4,9,10] the results will be discussed in terms of extractable and nonextractable phosphorus in PBO fibers. Extractable phosphorus is defined as the phosphorus removed during the water Soxhlet extraction procedure, while nonextractable phosphorus is defined as requiring mechanical or chemical means to remove it from the fiber.

Extractable Phosphorus in PBO Fibers. With recognition of the possible presence of phosphorus-containing processing additives in manufactured PBO fibers, the Soxhlet extraction method was employed to separate free acid species from nonextractable phosphorus. Table 1 shows XRF results for the PBO fibers before and after Soxhlet extraction and the extracted solutions. Consistent with previous research, the 1st set of PBO fibers was found to contain about 0.38% phosphorus by mass. After Soxhlet extraction for 7 days, data from the 1st set of PBO fibers indicates that 75% of the phosphorus remained in the fibers. The phosphorus level in the 1st set of PBO fibers is consistent with PBO fiber analyses from previous research.[9,10] Additionally, the amount removed by Soxhlet extraction is consistent with the

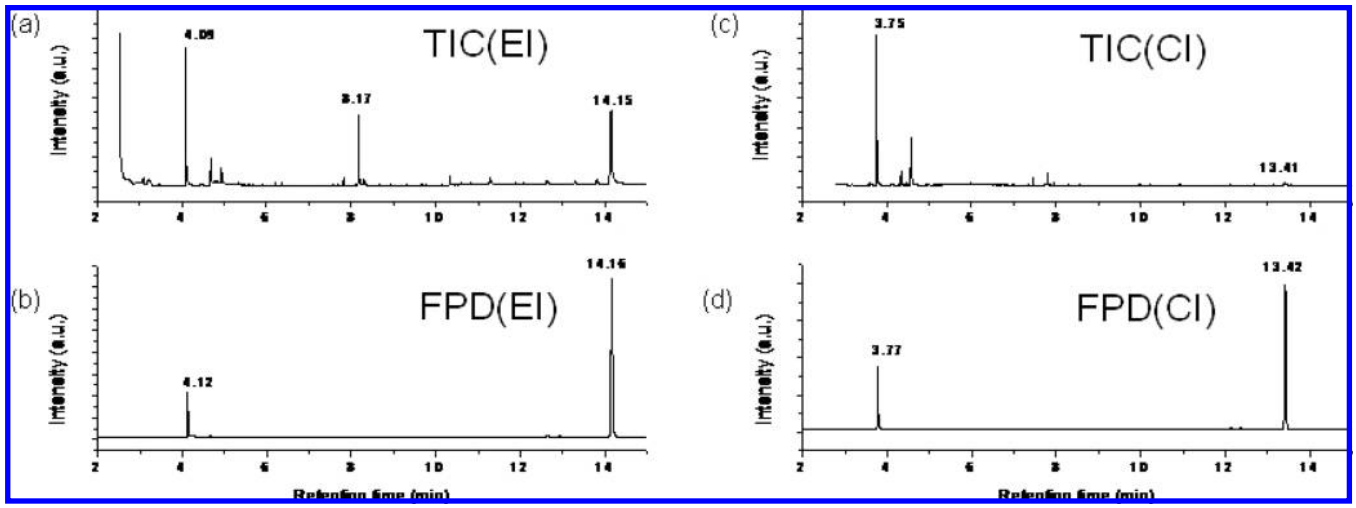

Figure 3. Total ion current (TIC) chromatograms (a) and (c) and parallel flame photometric detector (FPD) chromatograms (b, d) of methylated aqueous extract from PBO fibers under electron impact (EI) (a, b) and chemical ionization (CI) (c, d) test conditions. A.U. denotes arbitrary units of intensity.

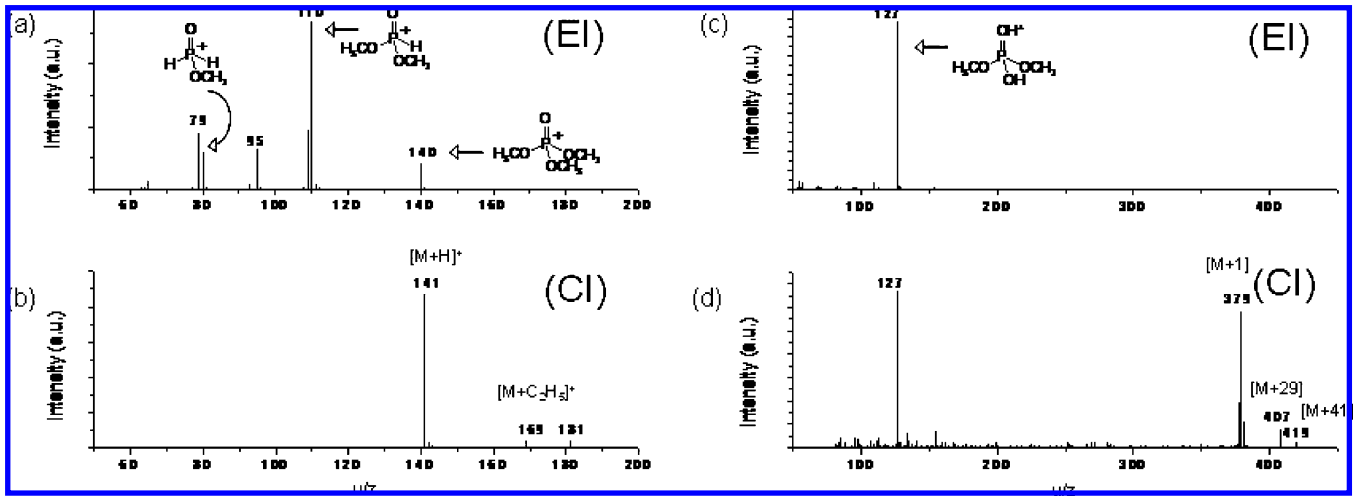

Figure 4. Electron impact (EI) and chemical ionization (CI) spectra of trimethyl phosphate (a, b) and long-chain alkyl phosphate (c, d). A.U. denotes arbitrary units of intensity.

quantity removed by supercritical fluid extraction.[9] Comparatively, the initial phosphorus levels in the 2nd and 3rd sets of PBO fibers were 16% and 37% lower, respectively, than the 1st set of PBO fibers. These reductions may reflect inconsistencies in the NaOH washing procedure during manufacturing or a change by the manufacturer to a more efficient washing process. Consistent with the 1st set of PBO fibers, the Soxhlet extraction procedure removed little or none of the residual phosphorus from the as received samples. Furthermore, a subsequent Soxhlet extraction of the 1st set of PBO fibers after they were damaged by crushing caused no additional reduction in the level of phosphorus, further suggesting that the remaining phosphorus is not extractable.

In the 1st set of PBO fibers, the aqueous extract was concentrated and acidified with HCl to convert any extracted acid salts to the free acid. An attempt was made to extract these phosphorus species into diethyl ether for the methylation procedure with no success. For the 2nd and 3rd PBO fiber samples, the extracted phosphorus containing species were also concentrated as describe in the Experimental Section and acidified with HCl. In a departure from the procedure used on the extractant from the 1st set of PBO fibers, a 1 mL portion of the concentrated extract was mixed with a 3:1 diethyl ether/ethanol mixture, methylated as described in the Experimental Section, and analyzed by GC/MS under electron impact (EI) and chemical ionization (CI) test conditions along with FPD and NPD detection.

The total ion current (TIC) chromatogram and the parallel FPD chromatogram are shown in Figure 3 for the samples run under EI and CI test conditions. In the FPD chromatograms (parts b and d of Figure 3), two peaks at retention times of 4.12 and 14.16 min under EI conditions and 3.77 and 13.42 min under CI conditions are shown that indicate phosphorus containing compounds. The EI and CI mass spectra of the first peak are shown in parts a and b of Figure 4. From Figure 4b, the characteristic ions parent + 1 u, parent + 29 u, and parent + 41 u observed under CI conditions indicate that the molecular mass of the first eluting phosphorus containing species is 140 u. The EI spectrum, which is consistent with the published spectrum of the trimethyl ester of phosphoric acid (CAS no. 512-56-1),[17] indicates the successive loss of two units of 30 u from the parent ion (140 u) and the parent − 1 u ion to form the fragment ions observed at

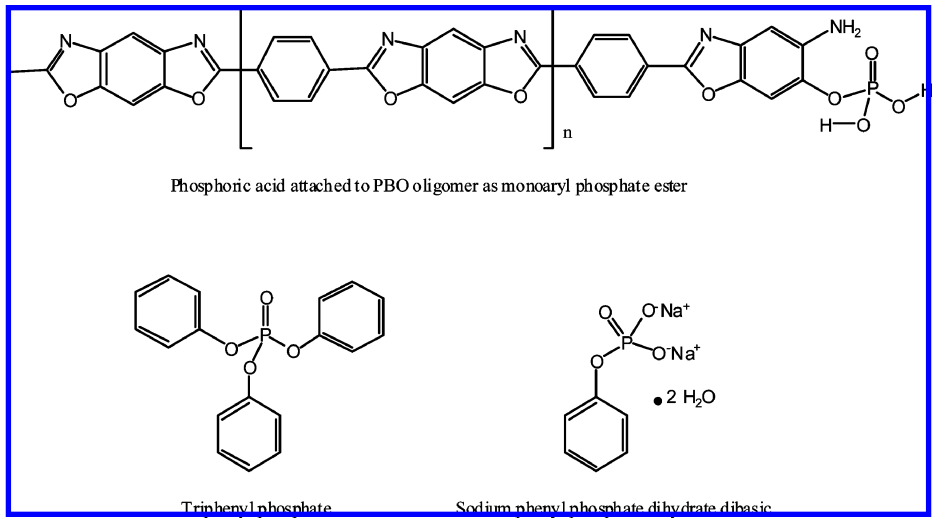

Figure 5. Chemical structure representation of phosphoric acid chemically bound to PBO oligomer as a monoaryl phosphate ester. To underscore the stability of the monoaryl phosphate ester bond, the chemical structures of triphenyl phosphate (a triaryl phosphate ester) and sodium phenyl phosphate dibasic dihydrate (a monoaryl phosphate ester), which are available commercially, are also shown.

110 u and 80 u and 109 u and 79 u, respectively. The losses from the parent ion have been shown to be exclusively linked to the elimination of the neutral species CH_2O.[17] Therefore, the EI and CI spectra of the first eluting peak indicate the presence of extractable phosphoric acid from the PBO fibers.

From Figure 4d, ions at 379, 407, and 419 u in the second eluted peak correspond to the characteristic ions mentioned above for CI molecular ion determination and indicate that the molecular mass of this species is 378 u. The absence of the corresponding molecular ion under EI conditions (Figure 4c) and the indication from parts b and d of Figure 3 that this compound contains phosphorus suggest that this species may be a phosphate ester with a long alkyl chain. The dominant fragment ion at 127 u can be assigned to the structure shown in Figure 4c, further supporting the identification of this species as a long alkyl chain, dimethylester phosphate, where the dimethyl ester groups on this trialkyl phosphate ester arise from the methylation procedure.

It is known that ethyl and higher alkyl phosphate esters undergo the classic McLafferty +1 rearrangement to eliminate the alkyl groups as a radical from the molecular ion.[18] Furthermore, the EI mass spectrum of the diethyl pentyl ester of phosphoric acid (DEPEPA, relative molecular mass = 224 u, CAS no. 20195-08-8) contains the corresponding rearrangement fragment ion at 155 u, which reflects the presence of the diethyl groups rather than the dimethyl groups indicated on the 127 u fragment ion found in Figure 4c. Successive losses of 28 u below the 155 u fragment ion are observed in DEPEPA that probably correspond to successive losses of the neutral species C_2H_4. These losses are not observed in Figure 4c. Finally, the published spectra of the trimethyl silyl (TMS) derivative of 1-dodecyl-d_{25} phosphate also exhibits the characteristic McLafferty + 1 rearrangement to eliminate the deuterated dodecyl alkyl group as a radical from the molecular ion.[19] From these observations, the second phosphate compound seems to be an octadecyl dimethyl ester of phosphoric acid. This identification indicates that octadecyl phosphate or the disodium salt of octadecyl phosphate is being used as a processing aid by the manufacturer.

It is worth noting that even though the semiquantitative XRF analyses of the 2nd and 3rd sets of PBO fibers before and after Soxhlet extracted showed little or no discernible differences in phosphorus levels, the extractant from the 2nd set of PBO fibers showed by GC/MS, one of the most sensitive analytical tools for detecting unknown compounds, the presence of extractable phosphoric acid and *n*-octadecyl phosphate. This indicates that, in these latter sets of PBO fibers, the majority of the residual phosphorus is nonextractable.

Nonextractable Phosphorus in PBO Fibers. Two theories have been put forth to explain the presence and nature of the nonextractable phosphorus. The first theory suggests that phosphoric acid may be trapped in microscopic voids that are known to exist along the length of the PBO fiber (see Figure 2). In the presence of moisture, the trapped phosphoric acid in these microscopic voids is suspected of lowering the localized pH in the PBO material surrounding them, thereby creating a localized environment conducive to hydrolytic degradation. The second theory suggests that the residual phosphoric acid, if present, may be chemically bound to the PBO polymer chain structure as a monoaryl phosphate ester (see Figure 5).

To address the first theory, a second extraction was performed on the 1st set of PBO fibers that had been previously extracted with water by the Soxhlet procedure. These fibers were cut into small pieces and ground with a mortar and pestle cooled by liquid nitrogen in an attempt to disrupt the microscopic voids and make them more accessible to moisture. Although a semiquantitative assessment of the damage caused by grinding the fibers was not obtained, XRF results for the cut and ground fibers did not show a decrease of the amount of phosphorus compared to the analysis after the first extraction (see Table 1). Consistent with these results, XRF results for the 2nd extracted solution from the 1st set of PBO fibers indicated the presence of phosphorus comparable to that of the water blank. This result suggests that either

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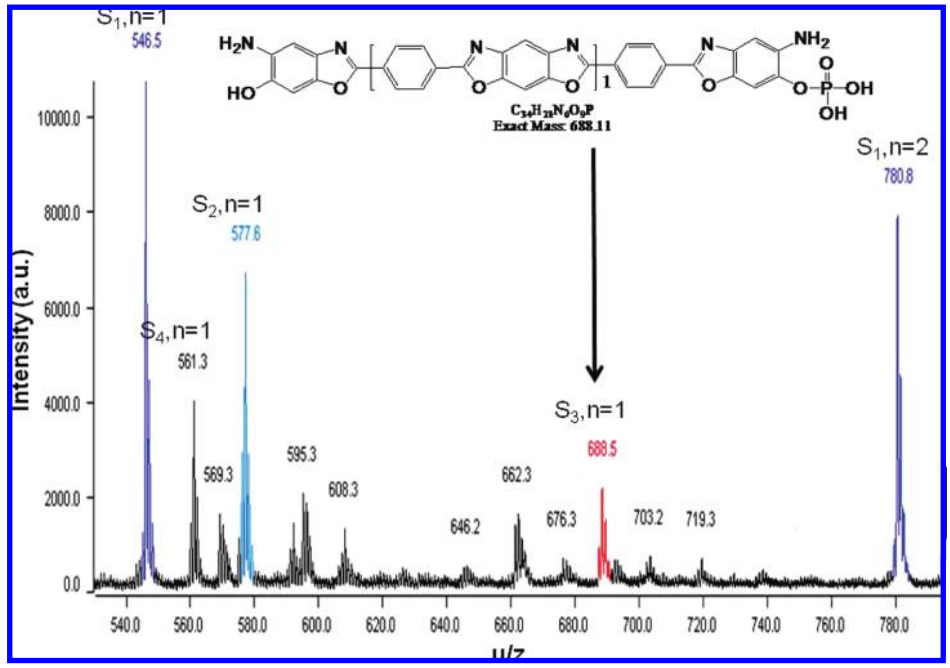

Figure 6. MALDI-TOF MS of low molecular mass model PBO oligomers. A.U. denotes arbitrary units of intensity.

the fibers were not sufficiently damaged by the crushing procedure or phosphoric acid is not trapped in the microvoids.

To pursue the second theory, the twice extracted fibers from the 1st set of PBO fibers were boiled for 7 days in 0.1 mol/L NaOH caustic solution. A small decrease in the phosphorus level was observed by XRF. The boiling experiment was repeated with 1 mol/L NaOH, with no observable change in phosphorus levels. To verify these results, the 2nd set of PBO fibers was boiled with 1 mol/L NaOH. Consistent with the 1st set of PBO fibers, the phosphorus level decreased slightly from 0.29% mass fraction to 0.27% mass fraction (see Table 1). A recheck of the 1st set of PBO fibers after boiling in NaOH revealed the presence of solid flakes in these fibers. Reanalysis of the twice Soxhlet extracted and twice NaOH boiled 1st set of fibers after removal of the flakes showed them to exhibit no change or a slight increase in the phosphorus level. The amount is also comparable to that found in the 2nd set of PBO fibers after Soxhlet extraction and treatment with 1 mol/L NaOH.

The solid flakes were found to contain sodium and silicon, with some phosphorus. After acidification of the solids and methylating the resulting aqueous solution, octadecyl phosphate, with no indication of phosphoric acid, was detected. The presence of this processing additive after boiling in the NaOH may reflect the increased solubility of disodium octadecyl phosphate in water relative to octadecyl phosphate. It should be noted that phosphorus was detected by XRF in the basic solutions from these NaOH treatments. Therefore, the NaOH treatments appear to lower the level of phosphorus in the fibers that have been previously subjected to the Soxhlet extraction procedure by converting the remaining octadecyl phosphate, which has limited solubility in water, to the more water-soluble disodium salt.

In a parallel investigation, the phosphorus levels in low-mass average molecular mass model PBO oligomers were investigated with the goal being to look for the presence of phosphorus containing species in these intractable model oligomers by MALDI-TOF MS. After extensive rinsing of the model PBO oligomers with water, the final phosphorus level by XRF was 1.4% (see Table 1). Soxhlet extraction of these oligomers reduced the phosphorus level to 0.062% mass fraction, with GC/MS identifying the phosphorus species in the aqueous extract as phosphoric acid detected as the trimethyl ester. Boiling these extracted oligomers in 0.1 mol/L NaOH for 7 days reduced the phosphorus level to 0.036% mass fraction. Again, the removed phosphorus species in the NaOH solution was identified as phosphoric acid.

PBO oligomers, because of the limited solubility of TA in the reaction medium, are preferentially capped with DADHB during the manufacturing process (see Figure 1). However, in the model compound studies performed by So et al. [see compounds (3) and (5) in ref 20], these researchers detected the presence of 4-(6-[4-(2-benzoxazolyl)phenyl]benzo(1,2-*d*;5,4-*d*′)-bisoxazol-2-yl) benzoic acid and 4-(2-benzoxazolyl)-benzoic acid when their model compounds were dissolved in methanesulfonic acid. These species are known to exist in the PPA reaction medium as aryl-acetyl PPA esters (see Figure 1) and can remain after the neutralization procedure as aryl-acetyl phosphate esters. These types of esters are known to be stable under neutral conditions while undergoing hydrolysis under basic conditions.[21] Therefore, it is probable that the additional phosphoric acid removed from our model systems by treatment with NaOH came from aryl-acetyl phosphate esters that are not typically found in processed PBO fibers.

A methodology was developed for identifying intractable PBO oligomers by testing the AF1, AF2, and AF3 model compounds using MALDI-TOF MS.[13] Analysis of the low-molecular mass PBO oligomers, synthesized as described in the Experimental Section, showed the presence of a peak at 688.5 u (see Figure 6). This compound was identified as being a mono-PBO phosphate ester

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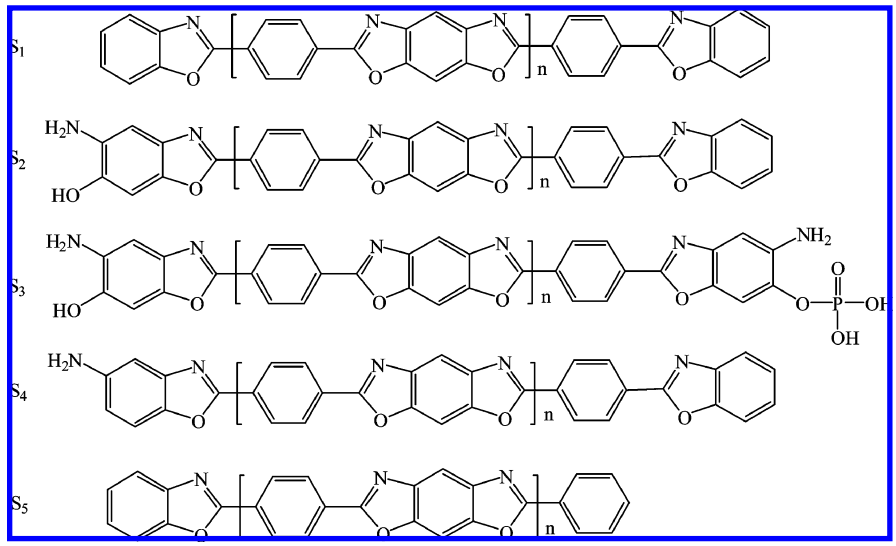

Figure 7. PBO oligomers identified in MALDI mass spectrum shown in Figure 6.

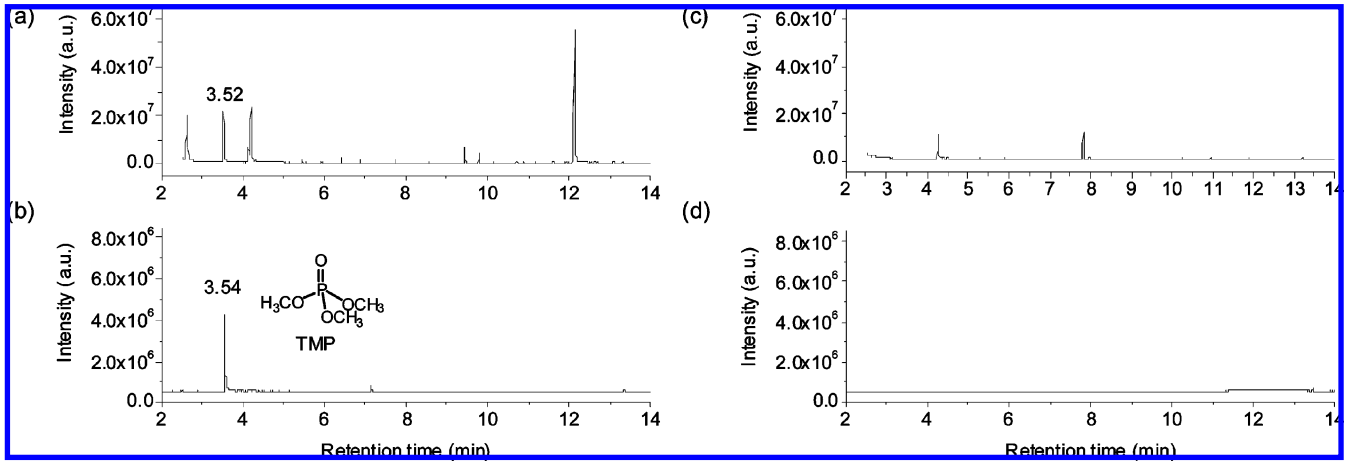

Figure 8. (a) Total ion chromatography (TIC) and (b) FPD spectrum of UV-exposed 2nd Caustic treated 1st PBO fiber Solution in the EI mode of GC/MS. (c) TIC and (d) FPD spectrum of UV-exposed water blank in the EI mode of GC/MS. A. U. denotes arbitrary units of intensity.

(an aryl-phosphate) that differs structurally from the aryl-acetyl phosphate ester discussed above. The other compounds identified from peaks in Figure 6 are shown in Figure 7. Reanalysis of the solids by MALDI-TOF MS showed that the compound at 688.5 u was not removed by Soxhlet extraction. Interestingly, this compound was not removed by boiling the solid oligomers with 0.1 mol/L NaOH caustic solution.

With note of the consistency of the model PBO oligomer results with those of the PBO fibers, the apparent stability of at least some of the nonextractable phosphorus to NaOH treatment is surprising since the working hypothesis considers the phosphorus to be chemically bound in the PBO oligomers as phosphate esters and phosphate esters can be hydrolyzed under alkaline conditions.[22] To investigate this further, the model compound TPhP (see Figure 5) was refluxed in a 1 mol/L NaOH solution for 7 days. After the solution was concentrated and methylated, 95% of the converted TPhP was found to be in the form of the dimethyl ester of monophenyl phosphate (DMPhP), with only 4.3% being converted to TMP.[13]

To verify this surprisingly low conversion of TPhP to TMP, sodium phenyl phosphate dibasic dihydrate (DNaPhP) (see Figure 5) was refluxed in a 1 mol/L NaOH solution for 7 days. The conversion from DNaPhP to the trisodium phosphate salt (TNaP), as reflected in the methylated products of TMP and DMPhP by GC/MS, was less than 2%. A similar experiment in a 1 mol/L $NaOCH_3$ solution resulted in a slightly higher conversion of 6.9% of DNaPhP to TMP.[13] The results indicate that if the nonextractable phosphorus is chemically bound to the PBO polymer as the monoaryl phosphate ester (see Figure 5), it may be partially stable to the NaOH solutions that are commercially used to effect its removal.

From the above results, sodium phenyl phosphate dibasic dihydrate (DNaPhP) was converted to the acid, monophenyl phosphate, using an HCl solution with a final pH of 4. This solution was then placed in a sealed container and irradiated with UV light (sealed chamber approach). The conversion of monophenyl phosphate to phosphoric acid, as measured by the presence of TMP by GC/MS, was completed within 24 h.[13] These results indicate that if the nonextractable phosphate is in the form of aryl-phosphate esters it may be removed by placing the fibers in an

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acidic medium and exposing it to UV radiation. After the 1st set of PBO fibers were Soxhlet extracted twice and washed with 0.1 and 1 mol/L NaOH solution for 7 days, they were washed with pH 4 HCl aqueous solutions and divided into three portions. Each portion was placed in an aqueous medium acidified to pH 4 by HCl and irradiated with UV for 25 h. The acid medium was replenished as needed to keep the sample from becoming dry (open chamber approach). The acid mediums were combined, concentrated, and tested for TMP, with very little being detected.

The 2nd set of PBO fibers that had been Soxhlet extracted and treated with 1 mol/L NaOH solutions for 7 days each were treated with pH 4 aqueous solutions. Following the results on the DNaPhP model compound study, the fibers and acidic solution were placed in a sealed system that has been described in the Experimental Section. GC/MS analysis of the aqueous solution indicated the presence of significant amounts of phosphoric acid in the form of trimethylphosphate (see Figure 8). The companion XRF analysis (see Table 1) indicates a decrease in the phosphorus level of the acid-treated and UV-exposed fibers by the closed system.

CONCLUSIONS

The data presented herein indicate that some free phosphoric acid is present in PBO fibers with a significant portion of the extractable phosphorus being *n*-octadecyl phosphate (either as the diacid or the diacid salt) that had been added as a processing aid. This result underscores the need to go beyond elemental analysis and determine the chemical identity of the residual phosphorus in the PBO fibers. The slight to moderate decrease in the residual phosphorus levels between the 1st set of PBO fibers and the 2nd and 3rd sets of PBO fibers suggests a possible change in the manufacturing process to better remove readily extractable phosphorus from the PBO fibers. With this potential reduction in residual phosphorus, the 2nd and 3rd PBO fiber sets indicate that the primary remaining phosphorus is chemically bound to the PBO oligomers, possibly in the form of monoaryl phosphate esters that are resistant to effective removal by washing with NaOH. MALDI-TOF MS of low mass average molecular mass PBO oligomers synthesized in a manner consistent with the manufacturing process supports the presence of monoaryl phosphate esters in PBO fibers. Subsequent studies of triphenyl phosphate and monophenyl phosphate also support the stability of monoaryl phosphates to NaOH treatments. However, acid treatments of monophenyl phosphate resulted in its complete conversion to phosphoric acid. Consistent with this latter result, acid treatment of PBO fibers that had been previously Soxhlet extracted and NaOH treated showed that additional phosphorus could be removed from the fibers in the form of phosphoric acid in a closed system that minimizes the loss of HCl. Interestingly, So et al.[7] deduced the presence of a monoaryl phosphate ester attached to PBO oligomers from their model compound studies using NMR. Consistent with the findings in this article, they observed that by placing one drop of water on the sample, the phosphate they deduced in the model compound studies as being in the form of a monoaryl phosphate slowly hydrolyzed under acid conditions.

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